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(54) Title: DELIVERY AND SCAVENGING AGENTS FOR COMBINATORIAL SYNTHESIS

(57) Abstract

Delivery and scavenging agents are provided for the combinatorial synthesis of organometallic compounds in a solution or suspension, where the agents are constructed from a solid support allowing for easy separation of unreacted reagents or unwanted materials from a synthesis reaction. Use of these solid supported agents also allows otherwise unfavorable reactions to be driven to completion by the use of large excesses of reactants and minimizes the chances for competing bimolecular side reactions in parallel or rapid serial synthesis.

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DELIVERY AND SCAVENGING AGENTS FOR COMBINATORIAL SYNTHESIS

This application is a continuation-in-part of pending U.S. Application No. 08/989,739, filed December 12, 1997, which in turn is a continuation-in part of U.S. Application No. 08/898,715, filed July 22, 1997, which in turn is a continuation-in-part of Serial No. 60/048,987, filed June 9, 1997. Application No. 08/898,715 is also a continuation-in-part of Serial No. 60/035,366, filed on January 10, 1997, which is a continuation-in-part of Serial No. 60/029,255, filed on October 25, 1996, which is a continuation-in-part of Serial No. 60/028,106, filed on October 9, 1996, which is a continuation-in-part of Serial No. 60/016,102, filed on July 23, 1996, however, this application does not claim the benefit of those applications. The teachings of all of the above applications are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention generally relates to the field of synthetic chemistry, including methodologies for synthesizing organometallic compounds and catalysts. In particular, this invention relates to solid supported agents and their use for the combinatorial synthesis of libraries of organometallic compounds.

BACKGROUND OF THE INVENTION

Ancillary ligand stabilized metal complexes (*e.g.*, organometallic complexes) are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs. The ancillary ligand system comprises organic substituents that bind to the metal center(s), remain associated with the metal center(s), and therefore provide an opportunity to modify the shape,

electronic and chemical properties of the active metal center(s) of the organometallic complex.

Certain organometallic complexes are catalysts for reactions such as oxidation, reduction, hydrogenation, hydrosilylation, hydrocyanation, hydroformylation, polymerization, carbonylation, isomerization, metathesis, carbon-hydrogen activation, cross-coupling, Friedel-Crafts acylation and alkylation, hydration, dimerization, trimerization, oligomerization, Diels-Alder reactions and other transformations. Organometallic complexes can be prepared by combining an ancillary ligand precursor with a suitable metal precursor in a suitable solvent at a suitable temperature.

One example of the use of organometallic complexes this is the field of single-sited olefin polymerization catalysis. The active site typically comprises an ancillary ligand-stabilized, coordinatively unsaturated transition metal alkyl complex. Although a variety of such organometallic catalysts have been discovered over the past 15 years, the discovery process is laborious, entailing the individual synthesis of potentially catalytic materials and subsequently screening them for catalytic activity.

One method for improving the efficiency of the discovery process relies on methods of producing combinatorial libraries of compounds and screening the compounds within those libraries for catalytic activity using an efficient parallel or rapid serial detection method. Certain techniques of combinatorial synthesis of libraries of organic compounds are known. For example, Pirrung, *et al.* developed a technique for generating arrays of peptides and other molecules using, for example, light-directed, spatially-addressable synthesis techniques (U.S. Patent No. 5,143,854 and PCT Publication No. WO 90/15070). Fodor, *et al.* have developed automated techniques for performing light-directed, spatially-addressable syntheses preparing photosensitive protecting groups, masks and methods for gathering fluorescence intensity data (Fodor, et al., PCT Publication No. WO 92/10092). In addition, Ellman, *et al.* recently developed a methodology for the combinatorial synthesis and screening of libraries of derivatives of three therapeutically useful classes of organic compounds, including benzodiazepines, prostaglandins and ß-turn mimetics (see U.S. patent 5,288,514). Schultz, *et al.*, was the first to apply combinatorial chemistry

techniques to the field of material science (PCT application WO 96/11878, the teachings of which are incorporated herein by reference). More particularly, Schultz, *et al.* discloses methods and apparatus for the preparation and use of a substrate having thereon an array of diverse materials in predefined regions.

In order to use combinatorial methodologies in the discovery of new organometallic compounds such as catalysts one must contend with some of the shortcomings of conventional synthesis. For example, conventional solution phase synthesis of organometallic compounds is often accompanied by the formation or presence of impurities such as reaction by-products, products of competing side reactions and unused reagents, which should be removed. The complexities of having to carefully control the amounts of reagents added to each reaction and the need for subsequent purification or separation steps presents a potentially formidable problem in the combinatorial synthesis of organometallic compounds, possibly rendering it more time consuming and less cost effective than conducting traditional non-combinatorial synthesis.

Thus, in connection with synthesizing libraries of organometallic materials, there are two fundamental issues to be addressed, namely the ability to control reagent stoichiometries and separation of unreacted or unwanted materials from the synthesis of the desired compounds. More specifically, the ability to cleanly prepare the desired compounds in a minimum number of synthetic steps and without complicated isolation protocols is critical. This is especially so for catalysis, where traces of metal or nonmetal containing impurities can have adverse effects on the observed catalytic behavior or could possibly account for observed catalytic behavior.

One approach to the construction of combinatorial libraries of materials involves the use of insoluble solid supports from which a molecular precursor is attached and chemically modified until the desired product is achieved. Upon completion of the synthetic sequence, the products are separated from by-products and unused reactants by filtration, and then cleaved from the solid support, often in very high yield and purity. Additionally, the ease by which products may be separated from unwanted materials also obviates the need for precise control over reagent stoichiometries. This approach is employed in a synthesis technique, known

as the split pool method, which is described, for example in U.S. patent 5,663,046. See also, U.S. patents 5,679,773 and 5,639,603, both of which are incorporated herein by reference. These references do not disclose cleaving a molecule from a support to deliver a compound or fragment thereof to a solution or suspension to facilitate a chemical reaction, particularly a synthesis reaction.

In addition to the ease of isolation and purification of products, the solid supported reagent approach allows otherwise unfavorable reactions to be driven to completion by the use of large excesses of reactants and minimizes the chances for competing bimolecular side reactions. However, solid supported reagents also are known to have a number of disadvantages. For example, there are limitations with respect to the solvent(s) that can be used with a particular solid support because it may react with the solvent(s) in a destructive manner or may not interact with the solvent at all therefore restricting reactivity of molecules or compounds attached to. In the former case, some solid supports cannot withstand conditions required for the cleavage of a desired molecule or compound from the support. Additionally, in the former case certain molecules that have been synthesized on a solid support may be unable to withstand the conditions required for cleavage of the molecule. This may especially be the case for organometallic molecules synthesized on a solid support. An example of the latter case may be found when crosslinked polystyrene resin is used as a solid support in a synthesis, requiring the use of solvents that will swell the resin in order to expose a useful number of reactive sites on the polymer. It may also be difficult to characterize the compound or molecule attached to the solid support.

Solid supported ligand and metals have been studied for various applications (for example, see Hartley, F. R. Supported Metal Complexes (Reidel Dordrecht, 1984)). U.S. patent 4,647,708 discloses the use of solid supported metal catalysts in connection with the production of aldehydes and alcohols by hydroformylation/reduction reactions. U.S. patent 4,098,727 discloses other solid supported metals.

An alternative approach to the synthesis of libraries of organometallic compounds utilizing solid supported ligands and metals is described within this invention.

SUMMARY OF THE INVENTION

This invention provides compounds, compositions and methods for effectively synthesizing compounds, particularly by a combinatorial methodology. In addition to the ease of isolation and purification of products, the invention described herein allows otherwise unfavorable reactions to be driven to completion by the use of large excesses of reactants and minimizes the chances for competing bimolecular side reactions

The invention disclosed herein provides compounds, compositions and methods for delivering compounds to and scavenging compounds from a chemical reaction. Two general classifications of agents are disclosed and described herein: (1) Delivery Agents and (2) Scavenging Agents.

Delivery Agents, generally, are capable of delivering a compound or fragment thereof to a solution or suspension for use in a chemical reaction. Generally, the solution or suspension can contain reactants or reagents that will contact, react with and bind to the compound or fragment thereof being delivered. For example, a metal delivery agent of this invention is a reagent capable of delivering a metal atom or ion, which may be a partially or fully ligated metal, to a solution or suspension containing ligands or other reagents with which it may react to produce desired organometallic compounds. Also for example, a ligand delivery agent of this invention is a reagent capable of delivering a ligand to a solution or suspension containing metal complexes or other reagents with which it may react to produce desired organometallic compounds. In addition, the delivery agent can be capable of delivering as much of a compound to a solution as is required for a particular synthesis.

Scavenging Agents, generally, are capable of binding an unreacted or unwanted compound in the synthesis reaction thereby allowing removal of the unreacted or unwanted compound. For example, a metal scavenging agent is an agent capable of binding a partially or fully ligated metal, thereby separating it from the desired product(s). Also for example, a ligand-scavenging agent is a reagent capable

of binding unreacted ligands, thereby separating them from the desired product(s). Other solid supported scavenging agents may also be employed, such as agents that are capable of a binding non-metal by-products and impurities, thereby separating them from a desired product(s) in solution.

In one aspect, this invention provides a metal delivery agent comprising a solid support and a partially or fully ligated metal bonded to the solid support, wherein the metal is detached from the solid support and delivered into a solution during a chemical reaction. Here, the solid supported metal delivery agent will deliver only as much metal as there is ligand in solution, with the metal excess remaining attached to the solid support; thus, the desired product may be isolated easily, e.g., by filtration.

In another aspect, this invention provides a ligand delivery agent comprises a solid support and a ligand bonded to the solid support, wherein the ligand is detached from the solid support and delivered into solution during a chemical reaction. In this aspect, the solid supported ligand delivery agent will deliver only as much ligand as there is metal in solution, with the ligand excess remaining attached to the solid support; thus, the desired product may be isolated easily, e.g., by filtration. Optionally, the ligand to be delivered is a ligand or fragment thereof attached to a metal which is in turn attached to a solid support.

In yet another aspect, this invention provides a ligand-scavenging agent comprising a solid support and a metal atom or ion, such as a partially or fully ligated metal, bonded to the solid support, wherein the metal contacts, reacts with and binds to a ligand in a solution during a chemical reaction. Inversely, a metal-scavenging agent comprises a solid support and ligand bonded to the solid support, wherein the ligand contacts, reacts with and binds to a metal atom or ion, such as a partially or fully ligated metal, in a solution during a chemical reaction.

In another embodiment, the two classes of solid supported agents are complementary to one another and facilitate the parallel synthesis of solution phase libraries of organometallic molecules, such as catalysts, by obviating the need for precise control over stoichiometries of reagents and allowing for the facile separation of unwanted metal and nonmetal containing species from the desired product(s).

Thus, one object of the invention is to provide solid supported agents that deliver or scavenge fragments of a compound to assist in the formation of a desired compound in a solution or suspension, with the agents being easily separated from the reaction mixture containing the desired product by filtration.

In another aspect of this invention solid supported agents are provided, which will deliver only as much metal or ligand precursor as there is available ligand or metal, respectively, in solution. Thus, this invention provides methods for performing combinatorial synthesis experiments without the need to carefully measure stoichiometries.

This invention also provides methods for performing combinatorial synthesis experiments where the products can be isolated in a parallel or rapid serial manner.

This invention also provides agents that are capable of enabling a kinetically or thermodynamically challenged reaction to be driven toward completion.

This invention provides agents for the delivery or scavenging of compounds or species in reactions that are either kinetically or thermodynamically controlled.

The above and other aspects and advantages of the present invention will be apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates one embodiment of the metal delivery agents of the invention, with the metal delivery agent including a partially or fully ligated metal, ML_n, which is to be delivered to a synthesis reaction (e.g., a ligand in solution).

Figure 2 illustrates one embodiment of the metal-scavenging agents of the invention, with the metal scavenging agent including a ligating group that will react with and bind to a partially or fully ligated metal.

Figure 3 illustrates one embodiment of the ligand scavenging agents of the invention, with the ligand scavenging agent including a partially or fully ligated metal having a vacant coordination site.

Figure 4 illustrates one embodiment of the ligand delivery agents of the invention, with the ligand delivery agent having a ligand(s), L_s, which dissociates from the metal M and is delivered to give a metal-ligand compound in solution.

Figures 5a-5d are examples of polymers with ligating groups built into the polymeric backbone.

Figure 6 illustrates one embodiment of the preparation and use of a metal delivery agent of Figure 1.

Figure 7 illustrates an example of the use of the metal scavenging agent of Figure 2.

Figure 8 illustrates an example of the use of the ligand-scavenging agent of Figure 3.

Figure 9 illustrates an example of the use of a column of metal delivery agents.

Figure 10 illustrates the possible interrelationship between metal scavenging agents, metal delivery agents, ligand scavenging agents and ligand delivery agents.

Figure 11 illustrates ligating strategies using Merrifield resins.

Figure 12 illustrates use of crosslinked polystyrene for preparing delivery and scavenging agents.

Figure 13 illustrates the derivatization of substituted or unsubstituted 1,2- and 1,4-polydienes, which can be functionalized through 1,2 additions for use in this invention.

Figure 14 illustrates Merrifield-like halomethylated arenes attached to silica by simple condensation of the silyl-Z bonds (Z-Si; Z = Cl, Br, I, OR) with surface silanols, producing a species of this invention.

Figure 15 illustrates direct and indirect preparation of graft polymers containing ligating groups.

Figures 16a-16d illustrate some radical induced polymerizations that utilize a support as a scaffold for the initiator.

Figure 17 illustrates delivery and scavenging agents that employ ionic bonding.

Figure 18 illustrates part of Example 1.

Figure 19 illustrates preparation of polystyrene grafted with polydienes for metal scavenging and delivery.

Figure 20 illustrates use of polystyrene grafted with polydienes for metal delivery.

Figure 21 illustrates the preparation and use of polystryene-*N,N,N'*-trimethylethylenediamine (PS-TMEDA) resin.

Figure 22 illustrates the use of polystyrene-tris(2-aminoethyl)amine (PS-TREN resin).

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides compounds, compositions and methods for the synthesis of organometallic compounds and ancillary ligand-stabilized catalysts (e.g., homogeneous and heterogeneous catalysts) and libraries thereof. Preferably, the synthesis of such libraries is carried out in a spatially selective, simultaneous, parallel or rapid serial fashion.

As used herein, the term "catalyst" refers to a compound that speeds a chemical reaction or causes it to occur. Certain of the organometallic compounds will require "activation" prior to being catalytically active. Other organometallic compounds will be "activator-free catalysts" and will not require activation prior to being catalytically active.

Organometallic compounds are conventionally formulated as comprising a central metal atom or ion coordinated or bonded to other atoms, ions, or small molecules known as "ligands." Ligands are either organic (*e.g.*, aryl, alkenyl, alkynyl, cyclopentadienyl, CO, alkylidene, carbene) or inorganic (*e.g.*, Br^-, Cl^-, OH^-,

NO, etc.), and can be charged or neutral. The number of times an inorganic or organic moiety occurs as a ligand in a metal-ligand compound is generally indicated by the prefixes di, tri, tetra, *etc.* Multiple occurrences of complex organic ligands are indicated by the prefixes bis, tris, tetrakis, *etc.* Each site on the metal atom or ion can be bound to an anionic or cationic portion of the ligand or with a neutral, Lewis base part of the ligand.

As used herein, the term "ancillary ligand" is distinguished from a "leaving group ligand." An ancillary ligand generally remains associated with the metal center(s) as an integral constituent of the catalyst or organometallic compound. After the synthesis reaction forming the catalyst or organometallic compound ancillary ligands will be attached to the metal center(s). Ancillary ligands are defined according to the number of coordination sites they occupy and their formal charge. A leaving group ligand is a ligand or fragment thereof that is replaced in a ligand substitution or other reaction. A leaving group ligand can be replaced with an ancillary ligand or vacant coordination site(s).

Ancillary ligands can become leaving group ligands and vice versa depending on the embodiment of the invention being practiced. For example, in the forward reaction of L_x-M-L_y + L_z _ L_x-M-L_z + L_y the ancillary ligand(s) are L_x and L_z and the leaving group ligand is L_y. In the reverse reaction, the ancillary ligand(s) are L_x and L_y and the leaving group ligand(s) is L_z. Also as used herein, the term "partially or fully ligated metal" refers to the central metal atom or ion that has its coordination sphere either partly or completely full with one or more ligands, either ancillary or leaving group ligands. Generally, the ligand libraries in this invention are ancillary ligand libraries.

In most cases, the formalisms for assigning the charge on the ligand and the number of coordination sites it occupies are easily established and unambiguous. As with most chemical formalisms, there are examples where these assignments are subject to interpretation and debate. Generally, the concept of sites and charges is used both herein and in commonly assigned U.S. Application No. 08/898,715. For example, a dianionic ligand that occupies two coordination sites on the metal is a {2, -2}, with the first 2 being the number of sites occupied and the –2

being the charge of the ligand.

Generally, there are five basic parts to the compounds and compositions of this invention: solid supports, tethers, metals, ancillary ligands and leaving group ligands. As used herein, M represents the central metal atom or ion and L represents the one or more ancillary or leaving group ligands bonded to M. Different ligands are given different subscripts (e.g., a, b, c, etc. give ligands L_a, L_b, L_c, etc.). Also, depending on the exact species, it is possible that a single representation of L can be different molecules. For example, if the partially or fully ligated metal to be delivered, ML_n, is NiClBr, then M represents the metal nickel and L_n represents both chloride and bromide ligands, which are ancillary ligands.

The terms "ligand precursor" and "metal precursor" are also used herein. These terms are used in an embodiment of this invention where metal-ligand compounds are synthesized starting from an array of "metal precursor" compounds, adding a ligand or an ancillary "ligand precursor" to each element of the array to form the desired metal-ligand compounds, scavenging excess metal precursor, if any, using a metal scavenging agent of this invention or scavenging excess ligand precursor, if any, using a ligand scavenging agent of this invention or filtering off a ligand delivery agent. The inverse is another embodiment of this invention, namely metal-ligand compounds are synthesized starting from an array of ancillary "ligand precursor" compounds, adding a metal or "metal precursor" to each element of the array to form the desired metal-ligand compounds, scavenging excess metal precursor, if any, using a metal scavenging agent of this invention or scavenging excess ligand precursor, if any, using a ligand scavenging agent of this invention or filtering off a metal delivery agent. In another embodiment, one or more array of metal precursors can be employed in connection with one or more array of ligand precursors. Also, ligands can be delivered from a ligand delivery agent to an array of metal precursors or metals can be delivered from a metal delivery to an array of ligand precursors.

Various conjugations of the words "ligand" and "metal" are used herein, including "metal-ligand compound," which refers to a compound having at least one metal and at least one ligand. "Organometallic compounds" also generally refers to compounds having a metal and a ligand. As used herein, "organometallic

compounds" are distinguished from catalysts by their lack of useful levels of catalytic activity in an initial screening. This definition does not, however, preclude a compound which was initially identified as an organometallic compound without catalytic activity in reference to a certain class of reactions but which is later identified as having catalytic activity with a different class of reactions.

In addition to M and L, other abbreviations used herein are: "A" refers to an anion; "Q" refers to a cation; "Me" for methyl; "Et" for ethyl; "Bu" or "t-Bu" for tertiary-butyl; "n-Bu" for normal-butyl; "Ph" for phenyl; "mes" for mesityl; "DMF" for *N,N'*-dimethylformamide; "THF" for tetrahydrofuran; "LDA" for lithium diisopropylamide; "OTf" for triflate; "OTs" for tolsylate; "X" or "Z" for an anionic group, such as halide, alkoxide, etc.; "SiO_2" for silica; "J" for a leaving group other than a ligand leaving group; "Cp" for cyclopentadienyl, which can be substituted or unsubstituted; "bpy" for 2,2'-bipyridyl; "AIBN" for 2,2'-azobisisobutyronitrile; "BAr'_4" for the noncoordinating anion, tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate; "NCC" for noncoordinating cation; "NCA" for noncoordinating anion; "Tol" for toluene; "PS" for polystyrene; "PI" for polyisoprene; "PBD" for polybutadiene; "DAB" for diazabutadiene, generally; "COD" for 1,5-cyclooctadiene; "PS-PBD" for polystyrene-graft-polybutadiene copolymer; "PS-PI" for polystyrene-graft-polyisoprene copolymer; "TMEDA" for *N,N,N',N'*-tetramethylethylenediamine; "TREN" for tris(2-aminoethyl)amine; "PEG" for poly(ethylene glycol); "PS-PEG-Br" for bromine terminated polystyrene-graft poly(ethyleneglycol) copolymer; "PS-PEG-OMe" for methoxy terinated polystyrene-graft-poly(ethyleneglycol) copolymer; "PS-TMEDA" for polystyrene functionalized with *N,N,N'*-trimethylethylenediamine copolymer: "PS-TREN" for polystyrene functionalized with tris(2-aminoethyl)amine; "PS-TMPDA" for polystyrene functionalized with trimethyl-1,3-propanediamine;"DME" for dimethoxyethane; "n-BuLi" for normal-butyl lithium; and "NMR" for nuclear magnetic resonance spectrometry. Also herein, the specification will generally refer to a "solution," but those of skill in the art will appreciate that this term includes suspensions.

As used herein, a "substrate" is a material having a rigid or semi-rigid surface. In some embodiments, at least one surface of the substrate will be

substantially flat. In other embodiments, the substrate will be divided into physically separate synthesis regions. Division of the substrate into physically separate synthesis regions can be achieved with, for example, dimples, wells, raised regions, etched trenches, or the like. In still other embodiments, small beads or pellets may be provided on the surface by, for example, placing the beads within dimples, wells or within or upon other regions of the substrate's surface. Alternatively, the small beads or pellets may themselves be the substrate. An appropriate substrate can be made out of any material which is compatible with the processes intended to occur thereon. Such materials include, but are not limited to, organic and inorganic polymers, quartz, glass, silica, etc. The choice of an appropriate substrate for certain given conditions will be apparent to those of skill in the art.

The methods of the present invention provide for the assembly of libraries of organometallic compounds and catalysts using solid supported agents, both delivery and scavenging agents. In one embodiment, this invention provides a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligands or ligand precursors;

b) delivering a metal to each element of said array of ligands using a metal delivery agent to create an array of metal-ligand compounds; and

c) optionally, separating any unreacted metal by filtration.

The array that is initially provided could also be an array of metal delivery agents, and a ligand or ligand precursor is added to that array to form an array of metal-ligand compounds. In that embodiment, this invention provides a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of metal delivery agents;

b) adding one or more ligands to the array of metal delivery agents to create an array of metal-ligand compounds; and

c) optionally, separating any unreacted metal by filtration.

In another embodiment, this invention provides for ligand delivery agents in the synthesis of libraries of organometallic compounds. In this embodiment,

this invention provides for a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of metal precursors;

b) delivering a ligand to each metal of the array using a ligand delivery agent to create an array of metal-ligand compounds; and

c) optionally, separating any excess ligand by filtration.

Again, the array that is initially provided could also be an array of ligand delivery agents, and a metal or metal precursor is added to that array to form an array of metal-ligand compounds. In that embodiment, this invention provides a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligand delivery agents;

b) adding one or more metals to the array of ligand delivery agents to create an array of metal-ligand compounds; and

c) optionally, separating any unreacted ligand by filtration.

In addition to delivering metals, this invention provides for scavenging metals from a reaction using a solid supported metal scavenging agent. Thus, in a further aspect, this invention provides for a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligands or ligand precursors;

b) adding a metal to each element of said array of ligands to create an array of metal-ligand compounds; and

c) scavenging any excess of said metal from each element of said array of metal-ligand compounds using a metal scavenging agent.

This invention further provides for scavenging ligands from a reaction using a solid supported ligand-scavenging agent. Thus, in yet a further embodiment, this invention provides for a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligands or ligand precursors;

b) adding a metal to each element of said array of ligands to create an array of metal-ligand compounds; and

c) scavenging any excess of said ligand from each element of said array of metal-ligand compounds using a ligand-scavenging agent.

This invention also provides for scavenging undesired side products or other unwanted compounds from a reaction using a solid supported scavenging agent. Thus, in still a further aspect, this invention provides for a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligands or ligand precursors;

b) adding a metal to each element of said array of ligands to create an array of metal-ligand compounds; and

c) scavenging any side products or unwanted materials from each element of said array of metal-ligand compounds with a scavenging agent.

These methods are advantageously used in combination. For example, in the synthesis of an array of ligands, it is possible that unwanted materials result in side products. Instead of laboriously removing each unwanted material from each element in the array of ligands prior forming a metal-ligand compound, a metal delivery agent can be employed in excess to attach the desired ligand to the desired metal, with the excess metal delivery agent being filtered off. In a subsequent step, a scavenging agent can be employed to attach the unwanted materials, which are then filtered from the remaining desired product. Therefore, it can be seen how the solid supported agents of the present invention allow for the parallel or rapid serial synthesis of libraries of metal-ligand compounds (such as organometallic compounds) in a combinatorial manner.

Therefore, another aspect of this invention provides a method of making an array of metal-ligand compounds, the method comprising the steps of:

a) providing an array of ligands having more than one element;

b) reacting each element of said array of ligands with a metal delivery agent to create an array of metal-ligand compounds;

c) filtering said metal delivery agent from said array; and

d) contacting each element of said array with a scavenging agent.

In another embodiment, this invention provides a method of making an array of metal-ligand compounds using one or more columns, such as a method comprising the steps of:

a) providing an array of ligands;

b) passing each element of said array through a first column containing a metal delivery agent; and

c) passing each element of said array through a second column containing a scavenging agent.

In this embodiment, it is possible that the first and second columns are part of a single column that has the metal delivery agent in a top portion and the scavenging agent in the bottom portion, or that the delivery and scavenging agents are commingled in a column. Clearly those of skill in the art can envision variations to the use of columns for the scavenging and delivery agents.

Thus, the ability to use combinations of delivery and scavenging agents represents a powerful means of efficiently preparing highly pure organometallic compounds from the standpoint of allowing flexibility in the synthesis.

The arrays (or libraries) in this invention are typically segregated arrays of metals or ligands. The term "segregated" is used to mean that each metal or ligand in the array is separated from the other members of the array typically on a substrate. The invention herein could be used to make metal-ligand compounds one at a time. It is preferred that arrays of metal-ligand compounds be made in a parallel or rapid serial fashion. Thus, the term "array" is used herein to mean more than one compound, ligand, metal, ligand precursor, metal precursor, metal-ligand compound, etc. Also, the array does not have to be on a substrate. For example, numerous ligands could be in solution together, which would be an array of ligands not on a substrate. A metal delivery agent could then be added to that solution to form numerous metal-ligand compounds in the solution.

The invention comprises the ability to form an array of more than one, more specifically of between 10 and 10^6 different metal-ligand compounds at known

locations on a substrate. In certain embodiments, the array will comprise more than 50 different metal-ligand compounds at known locations on the substrate. In other embodiments, the array will comprise more than 100 or more than 500 different metal-ligand compounds. In still further embodiments, the array will comprise more than 1,000, more than 10,000 or more than 10^6 different metal-ligand compounds at known locations on the substrate. In order to form these metal-ligand arrays, the starting ligand or metal arrays generally comprise an equivalent number of compounds. Thus, the starting ligand or ligand delivery arrays of this invention will comprise between 10 and 10^6 different ligands, typically at known locations on a substrate. In certain embodiments, the starting ligand array will comprise more than 50 different ligands, typically at known locations on the substrate. In other embodiments, the starting ligand array will comprise more than 100 or more than 500 different ligands. In still further embodiments, the array will comprise more than 1,000, more than 10,000 or more than 10^6 different ligands, typically at known locations on the substrate. The same is true for starting metal arrays. Thus, the starting metal or metal delivery arrays of this invention will comprise between 10 and 10^6 different metals, typically at known locations on a substrate. In certain embodiments, the starting metal array will comprise more than 50 different metals, typically at known locations on the substrate. In other embodiments, the starting metal array will comprise more than 100 or more than 500 different metals. In still further embodiments, the array will comprise more than 1,000, more than 10,000 or more than 10^6 different metals, typically at known locations on the substrate.

Generally, an ancillary ligand comprises each element of the array to which one or more metal is added. There may be two or more ligands in each array. However, ligand precursors may also comprise each element of the array to which one or more metal is added. Similarly, a metal atom or ion, such as a fully or partially ligated metal, comprises each element of the array to which one or more ligand is added. However, metal precursors may also comprise each element of the array to which one or more ligand is added.

Therefore, the methods of the present invention, which provide for the assembly of libraries of organometallic compounds and catalysts from such ligand

arrays or from metal arrays, may be thought of as a method comprising:

(a) providing a first metal-binding ligand and a second metal-binding ligand on first and second regions of a substrate;

(b) delivering a first metal to the first metal-binding ligand and a second metal to the second metal-binding ligand to form first and second metal-ligand compounds;

wherein said first and second metals are delivered using at least one metal delivery agent.

In this aspect, the metal may be an atom, ion or a partially or fully ligated metal. Also, more than one metal delivery agent may be used so that different metals are delivered to different ligands or ligand precursors in the array. Also, the same method is can be repeated with ligand delivery agents, metal scavenging agents and ligand scavenging agents with the appropriate starting array.

The metal or ligand delivery or scavenging agents may be used by allowing a solution of reactants to come into contact with the particular agent for a period of time to allow the desired transformations or chemical reactions to take place and/or products to form. For example, ligands are assembled on the substrate by the step-wise addition or delivery of ligand fragments and the reagents necessary to couple those fragments, thereby forming the library of ligands. Once the ligands are synthesized, they are reacted with the metal to form metal-ligand compound products, with the products remaining in solution, typically. The products can then be easily separated from the agents by filtration. In instances where reactions involving delivery or scavenging agents and are either slow or reversible it may be advantageous to load the agents onto a column and elute with a solution containing reactants or a reaction mixture.

A metal delivery agent of this invention is generally composed of at least two parts, a solid support (1) and a metal (7), which may be a partially or fully ligated metal to be delivered ML_n. The metal delivery agent can include a third part, which is a leaving group ligand (5) that is between the solid support and the metal to be delivered. The metal delivery agent can also include a fourth component, which is a tether (3) (sometimes referred to as a "linker") that is between the leaving group

ligand and the solid support. Specifically, Figure 1 shows a solid support (1), bonded to a tether (3), which is bonded to a leaving group ligand (5), which is in turn bonded to the metal to be delivered, ML_n (7). Although a bidentate ligand is shown as the leaving group ligand (5) in Figure 1 and in the other figures, those of skill of art will appreciate that a bidentate ligand is not essential and any appropriate ligand, which are discussed below, may be used, depending on the specific embodiment being practiced. A metal delivery agent comprises a solid support and a partially or fully ligated metal bonded to the solid support, wherein the metal is detached from the solid support and delivered into a solution during a chemical reaction. The metal delivery agent can additionally comprise a tether disposed between the metal and the solid support, wherein the metal is detached from the tether and delivered into a solution during a chemical reaction, and wherein the metal is bonded to the tether at a first site on the tether and the solid support is attached to the tether at a second site on the tether. The metal delivery agent can additionally comprise a ligating group disposed between the tether and the metal, wherein the ligating group is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group, and wherein the metal is detached from the ligating group and delivered into a solution during a chemical reaction.

The preparation and use of such a metal delivery agent is depicted in Figure 6. As shown in Figure 6, a solid supported ligand (400) is reacted with a metal presursor complex L_cML_n resulting in the attachment of the metal species to be delivered ML_n to the leaving group ligand (5) to give the metal delivery agent (200), and one or more extra ligands L_c as the by-product(s). Optionally, this metal delivery agent can be used as is or can be chemically modified through, for example, the substitution or transformation of one or more of the coordinating ligands or by altering the oxidation state of the metal. Figure 6 depicts an example of the former where the ligand(s) L_n of the metal delivery agent (200) is synthetically transformed into a new ligand(s) L_b to give a different metal delivery agent (300). As further shown in Figure 6, the metal delivery agent (200 or 300) is, through a general route, used in various synthetic steps, coming into contact with a reactant molecule or molecules (L_m). These molecules may react with the metal to be delivered, thereby

displacing it from the solid support, for example, by substitution of the solid supported leaving group ligand with the ancillary ligand, L_m (which may be soluble) to form the desired metal-ligand compound designated L_m-ML_n (where metal delivery agent 200 is used) or metal-ligand compound L_m-ML_b (where metal delivery agent 300 is used). Preferably, the soluble ligand L_m is an element of an array of ligands. If the metal delivery agent is used in a molar amount equal to or in excess of the reactants in solution then the reaction will proceed only so far as there is reactant available, leaving unreacted metal, if any, bound to the solid support. The spent or partially spent metal delivery agent (450) is then separated from the products of the reaction by filtration and may even be recycled for later use.

A ligand delivery agent of this invention is comprised of at least two parts, a solid support (1) and the ligand L_a (9) to be delivered (see Figure 4). Additionally, the ligand delivery agent of this invention can include a tether (3) bonded between the solid support and the ligand. The ligand delivery agent can also include an ancillary group ligand (15) and a partially or fully ligated metal ML_k (7) disposed between the tether and the ligand to be delivered or disposed between the solid support and the ligand to be delivered. Of course, the ligand delivery agent need not include a partially or fully ligated metal and the ligand to be delivered may or may not be coordinated directly to the metal. The ligand to be delivered may also be a fragment of an ancillary ligand bound to the partially of fully ligated metal. The embodiment shown in Figure 4 illustrates a ligand delivery agent comprising a solid support (1) bonded to a tether (3), which is bonded to an ancillary group ligand (15) and a partially or fully ligated metal atom (7), which in turn is bonded to the ligand to be delivered (9). A ligand delivery agent comprises a solid support and a ligand bonded to the solid support, wherein the ligand is detached from the solid support and delivered into solution during a chemical reaction. The ligand delivery agent can additionally comprise a tether disposed between the ligand and the solid support, wherein the ligand is detached from the tether and delivered into a solution during a chemical reaction, and where in the ligand is bonded to the tether at a first site on the tether and the solid support is attached to the tether at a second site on the tether. The ligand delivery agent can also comprise a ligating group and a metal atom disposed

between the ligand and the tether, wherein the ligating group is bonded to the tether at one site on the ligating group and bonded to the metal atom at a second site on the ligating group, and wherein the metal atom is bonded to the ligating group at one site on the metal atom and bonded to the ligand at a second site on the metal atom, and wherein the ligand is detached from the metal atom and delivered into a solution during a chemical reaction.

Scavenging agents are also within the scope of this invention, including metal scavenging agents, ligand scavenging agents and other scavenging agents (e.g., for the scavenging of other unwanted by-products or impurities).

A metal scavenging agent is composed of at least two parts, a solid support (1) and a ligating group (15) capable of binding to a particular metal complex or fragment thereof (see Figure 2). Optionally, the metal scavenging agent can include a tether (3) that connects the ligating group to the solid support (which is shown in Figure 2). Specifically, Figure 2 depicts a solid support (1), connected to a tether (3), which is in turn connected to a ligating group (15). Use of metal scavenging agent of Figure 2 is depicted in Figure 7. In Figure 7, the metal scavenging agent (500) is allowed to come into contact with a solution containing an unused reactant (such as a metal precursor or a metal that is an element of an array of metal compounds) or unwanted metal containing species L_eML_d, so that the metal scavenging agent can selectively bind the metal, possibly through substitution of a ligand, L_e. The immobilized metal species (600) is then separated from the products of the reaction by filtration. A metal-scavenging agent comprises a solid support and ligand bonded to the solid support, wherein the ligand contacts, reacts with and binds to a metal atom or ion, such as a partially or fully ligated metal, in a solution during a chemical reaction. The metal-scavenging agent can additionally comprise a tether disposed between the ligand and the solid support, wherein the ligand is bonded to the tether at a first site on the tether and the solid support is attached to the tether at a second site on the tether.

The ligand scavenging agents of this invention are comprised of at least two parts, a solid support (1) and a binding or vacant or reactive site (11) (see Figure 3). Optionally, the ligand scavenging agents also have a tether (3), a ligating

group (15) or a partially or fully ligated metal (7). In the latter case, the binding or reactive site on the metal M is capable of binding to, or reacting with, an unused non-metal containing reactant or by-product of a reaction so as to immobilize this species. One embodiment of the ligand scavenging agents of this invention is shown in Figure 3, which depicts a solid support (1) bonded to a tether (3), which in turn is bonded to a ligating group (15), which in turn is bonded to a metal (7) having a vacant coordination site (11) that will bind or react with the ligand to be scavenged. Use of the ligand scavenging agent (700) of Figure 3 is shown in Figure 8, where the ligand to be scavenged L_f is immobilized by the ligand scavenging agent to give species 800, which can then be separated from the desired products of the reaction by filtration. A ligand-scavenging agent typically comprises a solid support and metal atom or ion, such as a partially or fully ligated metal, bonded to the solid support, wherein the metal contacts, reacts with and binds to a ligand at a vacant or reactive site on the metal, in a solution during a chemical reaction. The ligand-scavenging agent can additionally comprise a tether disposed between the metal and the solid support, wherein the metal is bonded to the tether at a first site on the tether and the solid support is attached to the tether at a second site on the tether. The ligand-scavenging agent can additionally comprise a ligating group disposed between the tether and the metal, wherein the ligating group is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group.

In accord with chemical principles, each bond is to a separate site on each portion of the atoms that make up the agent, whether it is a delivery or scavenging agent.

Metal and ligand delivery and scavenging agents (900, 1000, 1100, 1200) can share common design features (Figure 10). For example, they can contain an insoluble or swellable solid support, a ligating group or a leaving group ligand and a tether that connects the support to the ligating group. Thus, a metal scavenging agent (900) can be thought of as a metal delivery agent (1000) without the metal (which may be partially or fully ligated). Likewise, a ligand scavenging agent (1100) may be thought of as a metal delivery agent (1000) that does not release the metal, ML_n, under the particular set of reaction conditions, but rather has an open

coordination site (shown as a box in Figure 10) that binds a ligand L_a or non-metal containing species irreversibly. A ligand scavenging agent (1100) can be thought of as a ligand delivery agent without the ligand attached L_a. An agent therefore may have the ability to bind a metal (or a ligand) and subsequently release the metal (or ligand) depending on the reaction conditions employed. Likewise, it is also possible that under different reaction conditions a metal delivery agent (1000) may instead act as a ligand scavenging agent (1100) or vice versa. Alternatively, a ligand-scavenging agent may subsequently act as a ligand delivery agent.

The reversibility of an agent's ability to bind or release a metal or a ligand is fundamentally related to the position of equilibria, which can be dependent on the reaction conditions employed (shown in Figure 10). These potential interrelationships enable flexibility in the basic design elements of the delivery and scavenging agents. For example. a spent metal delivery agent may find use as a metal scavenging agent in another application and so forth.

In an alternative embodiment, a metal delivery agent can be loaded onto a column and eluted with a solution containing a reactant such as a ligand, as in Figure 9. As shown in Figure 9. the metal delivery agent (150) contains the partially or fully ligated metal to be delivered ML_n (7) attached to the metal delivery agent and packed in a column (100). The ligand to which the metal will be delivered, L_g, is eluted through the column resulting in the desired metal-ligand compound, designated $L_nM\text{-}L_g$ in Figure 9. In this approach, as the eluent moves through the column the products become physically separated from spent solid supported reactants thus preventing back-reactions from taking place. Simultaneously, the reactants in the eluent are constantly exposed to a fresh excess of solid supported agents or reactants, thus helping the reaction, which may be equilibrium limited, to be driven to completion. Combinations of delivery or scavenging agents can also be loaded into a column in series or possibly as an admixture, thereby allowing multiple transformations leading to a desired product such as a catalyst to take place in succession on a single column.

As discussed above, there are five basic parts to the agents of this invention: solid supports, tethers, metals, ancillary ligands and leaving group ligands.

Many solid supports can be used to provide an insoluble or soluble framework for the delivery or scavenging agents disclosed herein. The solid support may also swell in the presence of one or more solvents. It is possible, therefore, for the solid support to be soluble under one set of conditions and insoluble under a different set of conditions (conditions include, e.g., temperature, solvent, etc.). Solid supports, called "synthesis supports" in commonly assigned application 08/898,715, can depending on the material be a porous, textured, or solid material, and may be flat or in the form of beads or any other geometric shape. Synthesis supports comprise, for example, functionalized polystyrene, polyacrylamide and controlled pore glass are known in the art. Jones, J., "Amino Acid and Peptide Synthesis," Oxford Science Publications, Oxford, 1992; Narang, S., Ed., "Synthesis and Applications of DNA and RNA." Academic Press, Inc., New York, 1987, and references therein which are herein incorporated by reference. Additionally, methods appropriate for functionalizing substrates are also appropriate for functionalizing materials intended for use as synthesis supports. Solid supports may be chosen from the group consisting of silica, functionalized silica, alumina, functionalized alumina, polymers (crosslinked or not), organic polymers which are amenable to functionalization or are already functionalized, polystyrene onto which polymers have been grafted, polysiloxanes, poly(ethylene glycol)s (PEG's), polyamines, polysulfides, sapphire, macroreticular resins, poly(propylene glycol)s (PPG's), inorganic solids, zeolites, clays, dendrimeric materials, quartz, silicon, metals, TEFLON, etc.

Tethers are molecules that link the solid support to the ligating groups, the ligand or the metal. Tethers, called "linkers" in commonly assigned application 08/898,715, may be chosen from the group consisting of organic molecules, polymers, inorganic molecules, solid state inorganic materials, partially or fully ligated metal complexes or fragments thereof, etc. Tethers may also be a natural extension of the ligating group or solid support used.

M is a metal atom or ion and can be chosen from any of the metals of the Periodic Table of Elements. Typically the metal is chosen from the group consisting of Groups 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 or Lanthanides or Actinides of the Periodic Table of Elements. The metal is chosen from the group

consisting of Al, Ga, In, Sn, V, Nb, Mn, Tc, Re, Fe, Ni, Pd, Pt, Rh, Ru, Ir, Cd, Co, Cr, Cu, Ag, Au, Mo, W, Os, V, Ti, Zr, Ta, Hf, Zn, Hg, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, Li, Na, Mg, Ca and mixtures thereof.

The present invention may utilize all ligands that are capable of binding metal ions. Ligand characteristics that can be varied include, but are not limited to, the number of coordination sites on the metal which the ligand can occupy, the charge and electronic influence of the ligand, the geometry imposed on the metal by the ligand, the geometry imposed on the ligand by the metal. A plethora of metal-binding ligands are known in the art and other ligands and ligand parameters amenable to variation using the methods of the instant invention will be apparent to those of skill in the art. For example, Collman, J.P., et al., Principles and Applications of Organotransition Metal Chemistry, University Science Books, California, 1987, and references therein which are herein incorporated by reference.

More specifically, the ancillary ligand binds to the metal center. The nature of the interaction between a ligand and a metal the delivery and scavenging agents of this invention may be physical or chemical adsorption to a surface, or through coulombic, ionic or covalent bonding, including Van der Waals, London, dipole-dipole and induced dipole-dipole interactions. Although lower numbers of coordination sites occupied by the ancillary ligand are typically preferred, embodiments utilizing larger numbers of coordination sites are not precluded. When the number of coordination sites is three or greater, the metal-ligand compound formed using this invention can have more than one geometry. In another embodiment, the coordination sites of the ancillary ligand are 1, 2, 3 or 4, and the charge on the ligands are 0, -1, -2, -3 or -4. Other ancillary ligands include those wherein the charge is greater than the number of sites it occupies. Due to the nature of their structure, certain ligands will have more than one possible coordination number and/or more than one possible charge. For example, a ligand's charge and/or coordination number can be different when it is bound to different metals such as an early- or a late-transition metal ion. By way of further example, a ligand which is deprotonated under strongly basic conditions, e.g., n-butyllithium, and contacted with

a metal ion can have a different coordination number and/or charge than the same ligand has when reacted with a metal ion under milder conditions.

Examples of ligands that can be used in the present invention include, but are not limited to, the following:

(1) One-site, monoanionic ancillary ligands such as the Cp* within the compound $Cp^*MR_2^+NCA^-$ (wherein M represents the metal, R is an alkyl), and mono-Cp systems in combination with methylaluminoxane (MAO);

(2) Two-site, dianionic ancillary ligands, which include, for example, bis-Cp systems (referred to in U.S. Patents Numbers 4,752,597 and 5,470,927, the teachings of which are incorporated herein by reference); mono-Cp systems where a heteroatom based ancillary ligand occupies the second site (referred to in U.S. Patent No. 5,064,802, the teachings of which are incorporated herein by reference); non-Cp, bis-amide systems (referred to in U.S. Patents Numbers 5,318,935 and 5,495,036, the teachings of which are incorporated herein by reference); and bridged bis-amido ligands and Group IV catalysts stabilized by ligands (referred to in *Organometallics* 1995, 14:3154-3156 and *J. Am. Chem.* 1996, 118:10008-10009, the teachings of which are incorporated herein by reference);

(3) Two site, monoanionic ancillary ligands including, for example, $Cp(L)CoR^+X^-$ and related systems (referred to in WO 96/13529, the teachings of which are incorporated herein by reference);

(4) Two site, neutral ancillary ligands, such as diazabutadiene ligands used in Ni^{2+} and Pd^{2+} catalytic systems. See, for example, Johnson, et al., *J. Am. Chem. Soc.*, 1995, 117:6414-6415 and WO 96/23010, the teachings of which are incorporated herein by reference;

(5) Three site, neutral ancillary ligands;

(6) Three site, monoanionic ancillary ligands;

(7) Three site, dianionic ancillary ligands;

(8) Three site, trianionic ancillary ligands;

(9) Four site, neutral, monoanionic and dianionic ancillary ligands; and

(10) Ancillary ligands where the charge is greater than the number of sites it occupies, for example, U.S. Patent No. 5,504,049, the teachings of which are

incorporated herein by reference).

Ligands which are used in practicing the instant invention include as part of their the binding domain of their structural motif groups such as. for example, alkyl, carbene, carbyne, cyanide, olefin, ketone, acetylene, allyl, nitrosyl, diazo, dioxo, disulfur, diseleno, sulfur monoxide, sulfur dioxide, aryl, heterocycles, acyl, thiocarbonyl, carbonyl nitrogen, oxygen, sulfur, phosphine, phosphido and hydride. Additional atoms and groups comprising a metal-binding domain are known in the art and are useful in practicing the instant invention. See, for example, Collman, J.P., et al. Principles and Applications of Organotransition Metal Chemistry, University Science Books, California, 1987, and references therein which are incorporated herein by reference.

As explained above, the libraries of ancillary ligands are made using combinatorial chemistry formats. Within the library, a wide range of ligand characteristics can be varied. Characteristics which are variable across the library include, for example, the ligand's bulk, electronic character, hydrophobicity/hydrophilicity, geometry, chirality, the number of coordination sites on the metal that the ligand occupies, the charge on both the ligand core and its substituents, and the geometry the ligand imposes on the metal.

Bi-, tri- and tetra-dentate ligand systems that lend themselves to combinatorial synthesis can be constructed, for example, from the following ligand fragments that are listed according to their charge.

The following ligands may be used in this invention:

1) Neutral ligands including, but are not limited to, amines ($R_1R_2R_3N$), phosphines ($R_1R_2R_3P$), arsines ($R_1R_2R_3As$), stilbines ($R_1R_2R_3Sb$), ethers (R_1R_2O), thioethers (R_1R_2S), selenoethers (R_1R_2Se) telluroethers (R_1R_2Te), ketones ($R_1R_2C=O$), thioketones ($R_1R_2C=S$), imines ($R_1R_2C=NR$), phosphinimine ($R_1R_2R_3P=NR$, $R_1P=NR_2$), phosphinidenes ($R_1R_2C=PR$), phosphine oxides ($R_1R_2R_3P=O$), phosphine sulfides ($R_1R_2R_3P=S$), pyridines, pyrazoles, imidazoles, furans, oxazoles, oxazolines, thiophenes, thiazoles, isoxazoles, isothrazoles, arenes, nitriles (R-C=N), isocyanides (R-N=C), acetylenes, olefins, sulfoxides.

2) Monoanionic ligands include, but are not limited to, amides

(R_1R_2N), phosphide (PR_1R_2), silyl ($SiR_1R_2R_3$), arsido (AsR_1R_2), SbR_1R_2, alkoxy (OR), thiolate (SR), selenate (SeR), tellurolate (TeR), siloxy ($OSiR_1R_2R_3$), cyclopentadienyl (C_5R_5), boratobenzenes($C_5BR_1R_2R_3R_4R_5R_6$), pyrazoylborates, carboxylate (RCO_2^-), acyl (RCO), amidates, alkyl, aryl, triflates ($R_1R_2R_3CSO_3^-$), thiocarboxylate (RCS_2^-), halide, nitrate, and the like.

3) Dianionic ligands include, but are not limited to, cycloctatetrenyl ($R_1R_2R_3R_4R_5R_6R_7R_8C_8^{2-}$), alkylidenes ($R_1R_2C$), borylides ($C_4BR_1R_2R_3R_4R_5$), imido (RN), phosphido (RP), carbolide, oxide, sulfide, sulphate, carbonate, and the like.

4) Trianionic ligands include, but are not limited to, alkylidynes (R-C=), P^{3-} (phosphides), Ar^{3-} (arsides), nitrides N^{3-}, phosphites.

Multidentate ligands can generally be constructed by bridging ligands through one or more of the pendent R-groups. Specific examples of bidentate neutral ligands {2,0} which may be constructed from the list of ligand fragments set forth above, include, but are not limited to, diimines (derived from two imines), pyridylimines (derived from a pyridine and imine), diamines (derived from two amines), imineamines (derived from an imine and an amine), iminethioether (derived from and imine and a thioether), imineethers (derived from an imine and an ether), iminephosphines (derived from an imine and a phosphine), bisoxazoline (derived from two oxazolines), diethers (derived from two ethers), bisphosphineimines (derived from two phosphineimines), diphosphines (derived from two phosphines) and phosphineamine (derived from a phosphine and amine). Other bidentate neutral ligand systems can be similarly constructed from the list of neutral ligands set forth above.

Bidentate monoanionic ligands {2,1} can be constructed by bridging a neutral ligand with a monoanionic ligand fragment from the lists set forth above. Examples include, but are not limited to, salen and other alkoxy imine ligands (derived from imine and alkoxy ligands), amidoamines (derived from an amide and an amine) and amidoether (derived from an amido and ether). Other bidentate monoamine ligands can be similarly constructed.

Bidentate dianionic ligands {2,2} can be constructed either by

combining two monoanionic ligands or a dianionic ligand and a neutral ligand. Specific examples include, but are not limited to, dicyclopentadienyl ligands (derived from two cyclopentadienyl ligands), cyclopentadienyl amido ligands (derived from a cyclopentadienyl and amide ligands), imidothioether ligands (derived from an imido and thioether ligands), imidophosphine ligands (derived from imide and phosphine ligands) and alkoxyamide ligands (derived from alkoxide and amide ligands). Other bidentate diamine ligands can be similarly constructed.

Bidentate ligands having charges greater than –2 can be constructed by combining monoanionic ligands with di- or tri-anionic ligands, or by combining two dianionic ligands. Examples include bisimido ligands (derived from two imide ligands), and carbyne ether ligands (derived from carbyne and ether ligands).

Tridentate neutral ligands {3,0} can be constructed by combining three neutral ligands from the list set forth above. Examples include, but are not limited to, 2,5-diimino pyridyl ligands (derived from two imine and one pyridyl ligands), triimidazoyl phosphines (derived from three imidazole ligands bonded to a central phosphorus atom), tris(pyrazoyl) alkanes (derived from three pyrazole ligands bonded to a central carbon atom). Other tridentate neutral ligands (e.g., {3,1}, {3,2}, {3,3}) can be similarly constructed.

In preferred embodiments, the coordination numbers (CN) of the ligand are independently 1, 2, 3 or 4, and the charge on the ligands are independently 0, -1, -2, -3, or -4. The ancillary ligand or ligand fragment need not be negatively charged, for example, positively charged ligands, such as, tropylium ($C_7H_7^+$), are also of use in practicing the present invention.

The presently preferred "families" of the coordination numbers and charges are: (i) CN = 2, charge = -2; (ii) CN = 2, charge = -1; (iii) CN = 1, charge = -1; (iv) CN = 2, charge = neutral; (v) CN = 3, charge = -1; (vi) CN = 1, charge = -2; (vii) CN = 3, charge = -2; (viii) CN = 2, charge = -3; (ix) CN = 3, charge = -3; (x) CN = 3, charge = 0; (xi) CN = 4, charge = 0; (xii) CN = 4, charge = -1; and (xiii) CN 4, charge = -2. In other preferred embodiments, the ancillary ligand has a charge which is greater than the number of coordination sites it occupies on a metal ion.

The R groups pendent from a ligand are chosen for the characteristics

which they impart to the organometallic compounds. Different R groups are given different subscripts (e.g., 1, 2, 3, etc. give R_1, R_2, R_3, etc.). R groups may affect the reactivity and stability of catalysts and organometallic compounds and may not bind directly and irreversibly to the metal center. The size and electronic nature of the R groups can be varied to alter the bulk around the metal center and the electronic properties of the metal-ligand compound. R groups which are chiral can impart chirality to the metal-ligand complex. Further, R groups are used to adjust the hydrophobicity/hydrophilicity of the ligand-metal compound.

The R groups on the ligands are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, arylalkyl, substituted arylalkyl, acyl, halogen, amino, cyano, nitro, hydroxy, alkoxy, alkylamino, acylamino, silyl, germyl, stanyl, siloxy, phosphino, aryloxy, aryloxyalkyl, substituted aryloxyalkyl, heteroaryl, substituted heteroaryl, heteroarylalkyl, substituted heteroarylalkyl, heterocycles, substituted heterocycles, heterocyclicalkyl, substituted heterocyclicalkyl S-aryl and S-alkyl mercaptans.

The term "independently selected" is used herein to indicate that the R groups, e.g., R_1, R_2, and R_3, can be identical or different (e.g. R_1, R_2 and R_3 may all be substituted alkyls or R_1 and R_2 may be a substituted alkyl and R_3 may be an aryl, etc.). Adjacent R-groups may be coupled to form cyclic structures.

A named R group will generally have the structure which is recognized in the art as corresponding to R groups having that name. For the purposes of illustration, representative R groups as enumerated above are defined herein. These definitions are intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

The term "alkyl" is used herein to refer to a branched or unbranched, saturated or unsaturated, monovalent hydrocarbon radical. When the alkyl group has from 1-6 carbon atoms, it is referred to as a "lower alkyl." Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. As used herein, the term encompasses "substituted alkyls." More particularly, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

"Substituted alkyl" refers to alkyl as just described including one or more functional groups such as lower alkyl, aryl, acyl, halogen (i.e., alkylhalos, e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, aryloxy, aryloxyalkyl, mercapto, both saturated and unsaturated cyclic hydrocarbons, heterocycles and the like. These groups may be attached to any carbon of the alkyl moiety.

The term "aryl" is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone. The aromatic ring(s) may include substituted or unsubstituted phenyl, naphthyl, biphenyl, diphenylmethyl and benzophenone among others. More particularly, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

"Substituted aryl" refers to aryl as just described including one or more functional groups such as lower alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The linking group may also be a carbonyl such as in cyclohexyl phenyl ketone.

The term "acyl" is used to describe a ketone substituent, --C(O)R, where R is alkyl or substituted alkyl, aryl or substituted aryl as defined herein.

The term "amino" is used herein to refer to the group $-NR_1R_2$, where R_1 and R_2 may independently be hydrogen, lower alkyl, substituted lower alkyl, aryl, substituted aryl or acyl. When an amino group is bonded to a metal through the nitrogen atom, it is referred to as an "amido" ligand.

The term "alkoxy" is used herein to refer to the --OR group, where R is an alkyl, substituted lower alkyl, aryl, substituted aryl, wherein the substituted alkyl, aryl, and substituted aryl groups are as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, phenoxy, substituted phenoxy, benzyloxy, phenethyloxy, t-butoxy, etc.

As used herein, the term "mercapto" defines moieties of the general

structure R_1—S—R_2 wherein R_1 and R_2 are the same or different and are alkyl, aryl or heterocyclic as described herein.

The term "saturated cyclic hydrocarbon" denotes groups such as cyclopropyl, cyclobutyl, cyclopentyl, etc. and substituted analogues of these structures.

The term "unsaturated cyclic hydrocarbon" is used to describe a monovalent nonaromatic group with at least one double bond, such as cyclopentene, cyclohexene, etc. and substituted analogues thereof.

The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are substituted by a heteroatom such as nitrogen, oxygen, sulfur, etc. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more nonaromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc., or benzo-fused analogues of these rings are defined by the term "heteroaryl."

"Heteroarylalkyl" defines a subset of "alkyl" wherein the heteroaryl group is attached through an alkyl group as defined herein.

"Substituted heteroaryl" refers to heteroaryl as just described wherein the heteroaryl nucleus is substituted with one or more functional groups such as lower alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc. Thus, substituted analogues of heteroaromatic rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "substituted heteroaryl."

"Substituted heteroarylalkyl" refers to a subset of "substituted alkyls" as described above in which an alkyl group, as defined herein, links the heteroaryl group to the nucleus.

The term "heterocyclic" is used herein to describe a monovalent saturated or unsaturated nonaromatic group having a single ring or multiple condensed rings from 1-12 carbon atoms and from 1-4 heteroatoms selected from nitrogen, phosphorous sulfur or oxygen within the ring. Such heterocycles are, for example, tetrahydrofuran, morpholine, piperidine, pyrrolidine, etc.

The term "substituted heterocyclic" as used herein describes a subset of "heterocyclics" wherein the heterocycle nucleus is substituted with one or more functional groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

The term "heterocyclicalkyl" defines a subset of "alkyls" wherein an alkyl group, as defined herein, links the heterocyclic group to the nucleus.

The term "substituted heterocyclicalkyl" defines a subset of "heterocyclic alkyl" wherein the heterocyclic nucleus is substituted with one or more functional groups such as lower alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

Most preferred ligands are selected from the group consisting of amines ($NR_1R_2R_3$), imines ($R_1N{=}CR_2R_3$), amides (NR_1R_2)$^-$, imides (NR_1)$^{2-}$, ethers (OR_1R_2), alkoxides and aryloxides (OR_1)$^-$, ketones ($R_1(C{=}O)R_2$), oxides (O)$^{2-}$, acetates (R_1CO_2)$^-$, thioethers (SR_1R_2), sulfides (SR_1)$^-$, sulfoxides ($R_1S(O)R_2$), phosphines ($PR_1R_2R_3$), phosphides (PR_1R_2)-, phospha(alkenes) ($R_1P{=}CR_2R_3$, $R_1R_2R_3P{=}CR_5R_6$), phosphine oxides ($R_1R_2R_3P{=}O$), phosphine sulfides ($R_1R_2R_3P{=}S$), phosphites ($P\{OR_1\}\{OR_2\}\{OR_3\}$), aminomethylphosphines ($R_1R_2NCHR_3PR_4R_5$), arsines ($AsR_1R_2R_3$), amidines ($R_1N{=}CR_1R_2NR_1R_2R_3$)-, nitriles (RCN), isonitriles (RNC), allyls ($R_1R_2CCR_3CR_4R_5$)-, cyclopentadienyl, alkyls, aryls, carbenes (R_1)$^{2-}$, carbynes (R_1)$^{3-}$, alkenes ($R_1R_2C{=}CR_3R_4$), alkynes (R_1CCR_2), sulfates (R_1SO_3)$^-$, sulfonamides ($R_1SO_2NR_2$)$^-$, silyls ($SiR_1R_2R_3$)$^-$ and halides. In these formulas, R is defined as above.

The ligands useful in this invention can be either symmetric or asymmetric with respect to the symmetry imposed by the backbone of the ligands and their substituents, and synthetic routes to such ligands will be apparent to those of skill in the art.

The anticipated though not necessarily actual mode of coordination

between a ligand and a metal species is presented in the examples that follow.

In further detail, chloromethylated, crosslinked polystyrene (1300 in Figure 11, where X = Cl), commonly referred to as Merrifield's resin, can be used as the solid support from which a variety of potential ligating groups can be attached. The chloride (or X = other halogen, tosylate or triflate substituted) benzylic carbon of (1300) can undergo substitution reactions with a variety of ligands yielding a variety of solid supported ligands with different site and charge {s,c} attributes.

Examples of solid supported ligands (1400, 1500, 1600, 1700, 1800, 1900, 2000 and 2100) prepared from halomethylated polystyrene (1300) are shown in Figure 11. In Figure 11, E represents an oxygen, sulfur, selenium or tellurium atom, G represents an nitrogen, phosphorus or arsenic atom, M = an alkali metal, Y = nothing; or M = an alkaline earth metal, Y = a halide, OTs, OTf or other leaving group, n = 1, 2, 3, etc., and each R is as defined above. The ligand precursors (1450, 1550, 1750, 1850, 1950, 2050 and 2150) can be prepared and coupled to the solid support by using standard organic techniques known to those skilled in the art. The solid supported ligands can be used to bind partially or fully ligated metal complexes reversibly or irreversibly as metal delivery or metal scavenging agents, respectively. Alternatively, solid supported metal complexes derived from (1300) (such as 1400-2100 of variations thereof) could be used in other applications as ligand delivery or scavenging agents.

In further detail of the making of the agents of this invention, polystyrene and polydienes can be used alone or be functionalized with discrete ligating groups for use as metal delivery and metal or ligand scavenging agents. For example, in Figure 12 crosslinked polystyrene (2200) can be used to bind metal complexes through the π-bonds of the arene (or can be functionalized with aryl species such as *p*-cymene for analogous metal binding) to give supported metal species (2300) (with the R groups as defined above). Crosslinked polystyrene (2200) can also be treated with n-BuLi to generate lithiated-PS (2400) (M. J. Farrall, J. M. J. Frechet *J. Org. Chem.* **1976**, *41*, 3877) and subsequently functionalized to yield a variety of solid supported ligands. For example, polystyrene bound amidines (2500) can be prepared from (2400) as shown in Figure 12. In addition, the lithiated

polystyrene can be treated with metal complexes such metal halides to yield solid supported metal alkyls (2600). The polystyrene bound metal alkyl complexes such as 2600 could be used as metal delivery agents in reactions with {2,1} ligands such as $R_1R_2NCH_2CH_2N(OTs)H$ (2700) to yield soluble metal amine-amide complexes (2800) and the partially or fully spent resin (2900) as a by-product. The solid supported ligands (2200-2600) may be reacted with appropriate metal complexes to prepare metal delivery agents and ligand scavenging agents. or may be used to scavenge metal species from solution. Additionally, the lithiated polystyrene (2400) can be treated with ligand precursors having one or more ionizable protons such as $H\text{-}L_n$ (2450), resulting in the deprotonation of $H\text{-}L_n$ and formation of a lithium salt of the ligand precursor. $Li\text{-}L_n$ (2455) and polystyrene (2200). Species 2455 can be further used in the preparation of metal complexes such as catalysts.

In another aspect, polymers such as substituted or unsubstituted 1,2-polydienes (3000) and 1,4-polydienes (3300) can be used to bind metal complexes through the π-bonds of the olefin backbones or they can be functionalized with a variety of potential ligating (as shown in Figures 13a and 13b respectively). For example, derivatives can be prepared by additions of HL_p across the double bonds in 1,2-polydienes (3000) by way of Markovnikov and Anti-Markovnikov additions to give products 3100 and 3200 respectively. Additions of HL_p across 1,4-polydienes (3300) result in the corresponding 1,2-addition products (3400). Derivatives 3100, 3200 and 3400, having L_p include those ligands and R groups as described above, can be prepared using standard organic synthetic methodology known to those skilled in the art. The advantages of this approach stem from the fact many different ligating groups can be introduced through additions across the diene backbones, and that by controlling the addition, whether occurring through a Markovnikov or Anti-Markovnikov pathway, the steric and electronic properties of the ligating group(s) can be controlled.

The surface of silica contains silanols (Si-OH) that can be used as points of attachment for ligands or as tethers from which ligands or polymers can be attached. The advantages of this approach are (i) that the surface concentration of silanols available for functionalization can be controlled by thermal pre-processing of

the silica or by varying the particle size (e.g., mesh) of the silica and (ii) that the silica does not need to be swelled in a solvent in order to be used, as is generally the case when using polymers such as cross-linked PS. Thus, a broader range of solvents (e.g., ones such as alcohols that ordinarily do not effectively swell polymers such as Merrifield resins) can be employed during the synthesis or purification of an organometallic compound. For example, a halomethylated arene (3600, X = Cl, Br, I; Z = Cl, Br, I, OR_x) can be attached to the silica (3500) by simple condensation of the silyl alkoxide bonds (Z-Si) with surface silanols (SiOH) to produce the Merrifield-like silica species (3700) and HZ (as shown in Figure 14). Unreacted silanols on the surface of the silica can be capped with a silanizing agent such as Me_3SiCl. The surface modified silica (3700) provides an inorganic based framework analogous to organic based Merrifield resin that can then be augmented with ligating groups L_h to produce silica supported ligands (3800) as exemplified in Figure 14. For example, transformations analogous to those depicted in Figure 11 (and elsewhere) may be performed with (3700). The silica based solid supported ligands can be used to bind metal species for subsequent use as delivery or scavenging agents.

Insoluble or soluble polymers and other supports may be used as scaffolds from which oligomeric or polymeric chains containing ligating groups can be grafted (as shown in Figure 15). Referring to Figure 15, the preparation of such solid supported polymer grafts (4100) can be achieved by either direct attachment of a polymer (4000) to the solid support (3900), or indirectly by chemically introducing an initiator, Int, to give a species (4200) (a solid supported initiator) from which a suitable monomers (4300) containing ligating groups (15) may be polymerized. The graft polymerizations of monomers from a solid support can be accomplished by cationic, anionic, radical, or metal-mediated processes. For example, many radical induced polymerizations are conceivable utilizing a solid support as a scaffold for the initiator (as shown in Figures 16a-16d). In Figures 16a-16d, n or m denotes the degree of polymerization. The shaded circles in Figures 16a-16d denote a solid support as discussed above. The substituents marked L_z on the substituted vinyl species (4600) represent any ligand as defined previously, and R is as defined above.

Radical polymerizations mediated by living (Figure 16a), free (Figure 16b), and chain transfer (Figure 16c) mechanisms as well as polymerizations of macromonomers (Figure 16d), can be used with a variety of olefinic monomers with potential ligating groups. Specifically, Figure 16a shows two general strategies for the living polymerization of substituted vinyl monomers (4600), where the substitutent L_z and R are as defined above. The substituted vinyl monomers are graft polymerized onto a solid supported initiator (4400) where J = NR_1R_2 or $CpTiCl_2$, possibly with the addition of heat, to produce the solid supported ligating group (4500). Alternatively, substituted vinyl monomers (4600) can be polymerized from a solid supported sulfonyl chloride group (4700) in the presence of a suitable metal catalyst (MCAT) such as CuCl(bpy), $RuCl_2(PPh_3)_3$, $NiCl_2(PPh_3)_2$, etc., possibly with the addition of heat, to produce solid supported ligands (4800) as shown in Figure 16a.

Substituted vinyl monomers can also be polymerized using free radical polymerizations as depicted in Figure 16b. Specifically Figure 16b shows the modification of an amino substituted solid support (4900) with an initiator (5100) yielding a solid supported initiator (5000). Species 5000 can then be used to initiate the polymerization of substituted vinyl monomers (4600), possibly with the addition of heat, to produce solid supported ligands (5200). One initiator (5100) is shown, but others known to those skilled in the art are possible. Alternatively, as shown in Figure 16c, a Merrifield resin or Merrifield-like species (5300) can be converted to a thiol derivative (5400) under basic conditions (^-OH) using thiourea (5500). The solid supported thiol species (5400) can then be used to polymerize substituted vinyl species (4600) in the presence of an initiator (such as AIBN) and possibly with the addition of heat to yield the solid supported ligands (5600). Alternatively, radical based polymerizations can be employed using a variety of initiators (designated Int) to prepare polymeric species with ligating groups L_z (5700) from substituted styrene monomers such as the para-substituted styrene macromonomers (5700).

Many initiators and conditions known to those skilled in the art can be used to carefully tailor the polymerization in preparing delivery and scavenging

agents for a particular application such as the synthesis of organometallic based catalysts.

Insoluble or soluble polymeric species including but not limited to crosslinked poly(vinyl alcohol), polyacryonitrile, poly(4-vinylpyridine), poly(amino acids), poly(nucleic acids), poly(ethylene glycol), and polydienes have amine, alcohol, nitrile, ester, amide, acid, phosphate, and olefinic groups, etc. built into the natural backbone of the polymeric chain that can bind metal complexes for use in the delivery and scavenging agents of this invention as solid supports, tethers or ligands (as shown in Figures 5a-5d). In Figure 5a the shaded circle denotes the solid support and in Figures 5a-5d, n refers to the degree of polymerization. Specifically, Figure 5a shows a polymer (5900) consisting of a polystyrene support (denoted by the shaded circle) to which poly(ethylene glycol) has been grafted. Figure 5b shows polyacryonitrile (6000); Figure 5c shows poly(4-vinylpyridine) (6100); and Figure 5d shows polybutadiene (6200). Clearly other soluble or insoluble polymeric species containing ligating groups built into the polymeric backbone and capable of binding partially or fully ligated metals also apply here.

Charged compounds may be bonded to solid supports by taking advantage of the coulombic attraction between anions and cations (as shown in Figure 17). In Figure 17 the shaded circles represent a solid support and the partial charges on species (6300), (6400), (6500), (6700), (6800) and (6900) are given by the encircled + and – signs. Of course, the charges may be monoanionic, dianionic, etc. or monocationic, dicationic, etc.

An ion paired species (6300) composed of a solid supported NCC and a negatively charged metal species ML_n can be reacted with a species (6400) consisting of a cationically charged ligand L_m whose charge is balanced by an anion A to produce a new species L_m-ML_n (6600). In this reaction the anion A of (6400) is exchanged for the negatively charged metal component ML_n of (6300) to give (6500) and (6600). In the reaction between (6300) and (6400) to give (6500) and (6600), species (6300) is a metal delivery agent. The reverse reaction, where (6500) reacts with (6600) to yield (6300) and (6400) can be viewed as a metal scavenging reaction where (6500) behaves as a metal scavenger.

Figure 17 also shows how the metal delivery agent (6700) can consist of a noncoordinating anion (NCA) bound to a solid support and a partially or fully ligated metal species ML_n which is negatively charged. The reaction of (6700) with a ion paired ligand species (6800), consisting of a negatively charged ligand, L_m, and a cation Q, can result in the formation of the desired metal species L_m-ML_n (6600) and the solid supported NCA, now ion-paired with the cation Q (6900). Of course, the reverse reaction between (6900), now a metal scavenging agent, and (6600) produces (6800) and the scavenged metal species (6700). It will be evident to those skilled in the art how ligand delivery agents and ligand scavenging agents can be prepared using variations of the ideas expressed in Figure 17.

EXAMPLES

The following examples illustrate a variety of the embodiments of the present invention.

As necessary, experiments were carried out in an inert atmosphere using nitrogen or argon as the inert gas and following practices standard to those of skilled in the art for these types of reactions (for example, see Shriver, D. F. The Manipulation of Air-Sensitive Compounds, 2nd ed. (New York : Wiley, c1986)). Elemental analysis was performed by QTI Inc., Whitehouse, NJ. NMR spectra were taken on a Bruker Avance™ 300 MHz, using XWINNMR software. Except where noted, all solvents were obtained from J.T. Baker, Inc. or Aldrich and used without further purification. Dry solvents were obtained from Aldrich in Sure-Seal™ bottles and used without further purification. Deuterated solvents were purchased from Aldrich or Cambridge Isotopes, Inc. and used as is or dried according to standard procedures published in Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 3rd Ed.*; Pergamon: New York, 1989. Merrifield resin and crosslinked polystyrene was purchased from Advanced Chemtech or Fluka. Metal complexes and compounds such as (DME)$NiBr_2$, $AlMe_3$, $CoCl_2$, $ZnCl_2$, $FeCl_2$, MeZnCl, $ZnMe_2$, and MeMgCl were purchased from Aldrich; $(PhCN)_2PdCl_2$ and $VCl_3(THF)_3$ were purchased from Strem Chemicals. (COD)PdMeCl was prepared according to

published procedures (see Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. Inorg. Chem. (1993), 32(25), 5769-78). The nomenclature for and syntheses of substituted diazabutadiene ligands (generally abbreviated DAB) are as reported in the literature (see G. V. Koten, K. Vrieze in Advances in Organometallic Chemistry, vol. 21, p 151). Novasyn TG bromo resin™ and Polyamine resin HL™ (PS-TREN) were purchased from NovaBiochem, Inc. and used as is. All other reagents were purchased from Aldrich and, if necessary, purified according standard procedures described in Perrin and Armarego (above).

EXAMPLE 1

This example describes the use of polystyrene-graft-poly(ethylene glycol) Resins (PS-PEG-OMe, 7100) for (1) the binding of $\{NiBr_2\}$ and $\{PdCl_2\}$ equivalents for (2) the preparation of organometallic precursors to olefin polymerization catalysts (7400 and 7500), as shown in Figure 18. In this approach, the PS-PEG-Br resin (7000) is first converted to the methyl ether derivative PS-PEG-OMe (7100) which is isolated. Species 7100 is then allowed to react with a source of a metal halide, $\{MX_2\}$ (M = Ni, X = Br; M = Pd, X = Cl) such as $(DME)NiBr_2$ and $(PhCN)_2PdCl_2$ using CH_2Cl_2/THF as a solvent for the nickel compound or toluene as a solvent for the palladium compound yielding the corresponding solid supported $\{MX_2\}$ species (7400 and 7500). In this reaction, species 7100 behaves as a metal scavenging agent wherein the PEG graft of 7100 is used as a chelating ligand that mimics and displaces the diether ligand on $(DME)NiBr_2$, or that displaces benzonitrile (PhCN) ligands on $(PhCN)_2PdCl_2$. The solid supported $\{MX_2\}$ species (7400 and 7500) are then reacted with a diazabutadiene compound $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$ (7600) in CH_2Cl_2 resulting in the displacement of the $\{MX_2\}$ fragment from 7400 or 7500 and the formation of the product $\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}MX_2$ (7700 or 7800) and the partially spent, solid supported $\{MX_2\}$ species (7900 or 8000). In this reaction, species 7400 and 7500 are used as metal delivery agents to prepare the catalyst precursors 7700 and 7800 respectively. Species 7100 also reacts with other compounds containing $\{MX_2\}$ and $\{MX_3\}$ fragments as is seen in the examples that follow.

Part 1 -- Preparation of PS-PEG-OMe.

Poly(ethylene glycol) bromoethyl-polystyrene resin (0.25 g, 0.83 mmol, 0.30 mmol/g loading of Br) was combined with KO^{t}Bu (0.47 g, 4.16 mmol) and taken up in 20 mL of a THF/MeOH solution (4:1 v/v) and the suspension was heated at 70 °C under an N_2(g) atmosphere for 15 h. After cooling to room temperature, the resin was filtered and washed sequentially with THF (3 x 15 mL), H_2O (2 x 15 mL), and THF (3 x 15 mL), and was dried in vacuo to afford 0.20 g of poly(ethylene glycol) methoxyethyl-polystyrene (PS-PEG-OMe) as a beige colored resin. Elemental analysis performed on this sample indicated a 96% displacement of bromide, corresponding to a residual loading of 0.02 mmol/g Br (0.13% by weight).

Part 2 -- Preparation of PS-PEG-OMe-{$NiBr_2$}.

Poly(ethylene glycol) methoxyethyl-polystyrene resin, PS-PEG-OMe, (0.22 g) and (DME)$NiBr_2$ (1.00 g, 3.66 mmol) were suspended in 20 mL of dry CH_2Cl_2 under an N_2(g) atmosphere in a solid phase reaction vessel and placed on a rotating shaker for 24 h. The resulting deep green resin was washed extensively with CH_2Cl_2 (10 x 20 mL) to afford 0.30 g of the product PS-PEG-OMe-{$NiBr_2$}. Analysis performed on this sample indicated a loading of 2.22 mmol/g based on Br analysis (35.53% Br) and 2.25 mmol/g based on Ni analysis (13.53%).

Part 3 -- Preparation of {(2,4,6-$Me_3C_6H_2$)$_2$DAB(Me)$_2$}$NiBr_2$ using PS-PEG-OMe-{$NiBr_2$}.

PS-PEG-OMe-{$NiBr_2$} resin (0.22 g, 0.48 mmol) and (2,4,6-$Me_3C_6H_2$)$_2$DAB(Me)$_2$ (0.10 g, 0.31 mmol) were taken up in 5 mL of dry CH_2Cl_2 under an atmosphere of N_2(g) and stirred at room temperature for 24 h. The resin was washed with CH_2Cl_2 (2 x 5 mL) to give a reddish-brown solution which was concentrated by rotary evaporation. The remaining solid residues were recrystallized from CH_2Cl_2/hexane to give 0.16 g of {(2,4,6-$Me_3C_6H_2$)$_2$DAB(Me)$_2$}$NiBr_2$ as a reddish-brown solid in 95% yield.

Part 4 -- Preparation of PS-PEG-OMe-{$PdCl_2$}.

A glass scintillation vial was loaded with PS-PEG-OMe (0.200 g) and treated with a solution of $(PhCN)_2PdCl_2$ (0.200 g, 0.52 mmol) in 11 mL of toluene and the resulting suspension was stirred for 22.5 h at 25 °C using an orbital shaker. The resin gradually darkenened over the course of the first few hours of reaction while the initially dark amber color of the supernatant was observed to bleach. By completion of the reaction the resin was a black color and the supernatant was faintly colored. The supernatant was then transferred away from the resin using a pasteur pipette and washed with toluene (5 x 5 mL) to remove any sequestered material from the resin. Each time the toluene was added the resin was agitated on the orbital shaker for a period of 5-10 min to allow adequate time for soluble materials to diffuse out of the resin before the supernatant was removed by pasteur pipette. The resin was then suspended in 5 mL of CH_2Cl_2 to allow and insoluble inorganic species to settle out and be removed by pasteur pipette. During the washings with toluene the supernatant became less and less colored until it was essentially colorless. The resin was then filtered over a frit and washed with diethyl ether (5 x 5 mL) allowing about 30-60 seconds of contact between the resin and ether with each wash before filtering. The black colored resin was then dried in vacuo overnight and analyzed for Pd and found to have a loading of 1.00 mmol/g (10.60% Pd). Yield: 0.239 g)

Part 5 -- Reaction of PS-PEG-OMe-{$PdCl_2$} with $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$.

In a small glass vial was placed 31 mg (0.031 mmol equivalents) of PS-PEG-OMe-{$PdCl_2$} followed by a solution containing 5.0 mg (0.016 mmol) of $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$ in 1.0 mL of CD_2Cl_2. The suspension was allowed to stir on an orbital shaker at 25 °C and the reaction was monitored by NMR. After a period of 1 hour the ^1H NMR showed significant loss of resonances for the free ligand and the appearance of resonances for $\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}PdCl_2$. In addition, a yellow crystalline solid was observed to precipitate from the reaction mixture, consistent with the formation of the sparingly soluble product

$\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}PdCl_2$. After 1 day additional yellow solids had settled from the reaction mixture and the ^1H NMR spectrum showed only resonances for the product.

Part 6 -- Preparation of PS-PEG-OMe-$\{CoCl_2\}$.

To a stirring suspension of PS-PEG-OMe (0.10 g) in 10 ml anhydrous CH_2Cl_2 and 1 ml anhydrous THF under nitrogen was added cobalt(II) chloride (77 mg, 0.60 mmol). After stirring at room temperature for 48 hrs., the mixture was filtered under an inert atmosphere and washed extensively with anhydrous CH_2Cl_2 (5 x 15 ml) to yield 0.154 g of PS-PEG-OMe-$\{CoCl_2\}$ as a sky-blue colored resin. Elemental analysis of this resin revealed a loading of 0.44 mmol/g based on cobalt (2.63% Co).

Part 7 -- Preparation of PS-PEG-OMe-$\{VCl_3\}$.

To a stirring suspension of PS-PEG-OMe (0.30 g) in 25 ml anhydrous CH_2Cl_2 under nitrogen was added $VCl_3(THF)_3$ (0.200 g, 0.54 mmol). After stirring at room temperature for 24 hrs., the mixture was filtered under an inert atmosphere and washed extensively with anhydrous CH_2Cl_2 (5 x 15 ml) to yield 0.450 g of PS-PEG-OMe-$\{VCl_3\}$ as a light burgundy colored resin. Elemental analysis of this resin revealed a loading of 1.38 mmol/g based on vanadium (7.03% V).

Part 8 -- Preparation of PS-PEG-OMe-$\{ZnCl_2\}$.

To a stirring suspension of PS-PEG-OMe (0.10 g) in 10 ml anhydrous CH_2Cl_2 and 1 ml anhydrous THF under nitrogen was added zinc(II) chloride (0.081 g, 0.60 mmol). After stirring at room temperature for 48 hrs., the mixture was filtered under an inert atmosphere and washed extensively with anhydrous CH_2Cl_2 (5 x 15 ml) to yield 0.162 g of PS-PEG-OMe-$\{ZnCl_2\}$ as a colorless resin. Elemental analysis of this resin revealed a loading of 0.50 mmol/g based on zinc (3.28% Zn).

Part 9 -- Preparation of PS-PEG-OMe-{$FeCl_2$}

To a stirring suspension of PS-PEG-OMe (0.30 g) in 10 ml anhydrous CH_2Cl_2 and 1 ml anhydrous THF under nitrogen was added iron(II) chloride (0.152 g, 1.80 mmol). After stirring at room temperature for 48 hrs., the mixture was filtered under an inert atmosphere and washed extensively with anhydrous CH_2Cl_2 (5 x 15 ml) to yield 0.200 g of PS-PEG-OMe-{$FeCl_2$} as a brown-orange colored resin. Elemental analysis of this resin revealed a loading of 0.71 mmol/g based on iron (3.97% Fe).

Part 10 -- Preparation of PS-PEG-OMe-{$TiCl_4$}.

In a glovebox, PS-PEG-OMe (0.525 g) was slurried in 5 mL THF. $TiCl_4(THF)_2$ (0.510 g, 1.53 mmol) was dissolved in THF (10 mL) and then added to the THF/resin mixture. The mixture was shaken overnight and then filtered. The dark red resin was washed with THF (3 x 30 mL), toluene (3 x 30 mL) and pentane (3 x 30 mL) and dried in vacuo (yield = 0.607 g).

Part 11 -- Preparation of PS-PEG-OMe-{$HfCl_4$}.

In a glovebox, PS-PEG-OMe (0.507 g) was slurried in 5 mL THF. $HfCl_4$ (0.525 g, 1.63 mmol) was dissolved in THF (10 mL) and then added to the THF/resin mixture. The mixture was shaken overnight and then filtered. The brownish- red resin was washed with THF (3 x 30 mL), toluene (3 x 30 mL) and pentane (3 x 30 mL) and dried in vacuo (yield = 0.595 g).

Part 12 -- Preparation of PS-PEG-OMe-{$NbCl_3$}.

In a glovebox, PS-PEG-OMe (0.302 g) was slurried in 5 mL CH_2Cl_2. $NbCl_3$(DME) (0.160 g, 0.55 mmol) was dissolved in CH_2Cl_2/THF (5 mL, 4/1 v/v) and was then added to the CH_2Cl_2/resin mixture. The resin became dark gray immediately. The mixture was shaken overnight and then filtered. The dark gray resin was washed with CH_2Cl_2 (3 x 30 mL), pentane (2 x 30 mL) and CH_2Cl_2 (2 x 30 mL) and then dried in vacuo (yield = 0.310 g).

Part 13 -- Preparation of PS-PEG-OMe-{$MoCl_3$}.

In a glovebox, PS-PEG-OMe (0.299 g) was slurried in 5 mL CH_2Cl_2. $MoCl_3(THF)_3$ (0.146 g, 0.35 mmol) was dissolved in CH_2Cl_2 (3 mL) and was then added to the CH_2Cl_2/resin mixture. The resin became red immediately. The mixture was shaken overnight and then filtered. The red resin was washed with CH_2Cl_2 (3 x 30 mL), pentane (2 x 30 mL) and CH_2Cl_2 (2 x 30 mL) and then dried in vacuo (yield = 0.329 g).

Part 14 -- Preparation of PS-PEG-Br-{Ta(=N(2,4,6-$(CH_3)_3C_6H_2$))Cl_3}.

In a glovebox, PS-PEG-Br (0.312 g) was slurried in 5 mL CH_2Cl_2. Ta(=N(2,4,6-$(CH_3)_3C_6H_2$))Cl_3(DME) (0.210 g, 0.41 mmol) was dissolved in CH_2Cl_2 (3 mL) and was then added to the CH_2Cl_2/resin mixture. The resin became orange after ten minutes. The mixture was shaken overnight and then filtered. The orange resin was washed with CH_2Cl_2 (3 x 30 mL), pentane (2 x 30 mL) and CH_2Cl_2 (2 x 30 mL) and then dried in vacuo (yield = 0.334 g).

EXAMPLE 2

This example describes the preparation of polystyrene-graft-polybutadiene (PS-PBD) and polystyrene-graft-polyisoprene (PS-PI) resins that can mimic the manner in which discrete diene ligands such as 1,5-cyclooctadiene (COD) binds to metals. The preparation of a solid supported polydiene such as polybutadiene or polyisoprene is accomplished by polymerizing the diene monomers directly off of a lithiated polystyrene solid support (Figure 19). Specifically, Figure 19 shows crosslinked polystyrene (8100) which is treated with n-BuLi to produce lithiated polystyrene in situ which is subsequently reacted with butadiene (R = H: 8200) or with isoprene (R = Me: 8300) to produce the graft copolymers PS-PBD (R = H: 8400) and PS-PI (R = Me: 8500). The graft copolymer resins, 8400 and 8500 are then treated with $(PhCN)_2PdCl_2$ or (COD)PdMeCl, resulting in the formation of the solid supported {$PdCl_2$} and {PdMeCl} equivalents, PS-PBD-{$PdCl_2$} (R = H, L = Cl: 8600), PS-PBD-{PdMeCl} (R = H, L = Me: 8700), PS-PI-{$PdCl_2$} (R = Me, L = Cl: 8800), and PS-PI-{PdMeCl} (R = Me, L = Me: 8900) as shown in Figure 19. Treatment of the {$PdCl_2$} loaded resins PS-PBD-{$PdCl_2$} (R = H: 9100) and PS-PI-{$PdCl_2$} (R = Me: 9200) with the diazabutadiene ligand (2,4,6-$Me_3C_6H_2)_2$DAB$(Me)_2$ (9600) results in the formation of {(2,4,6-$Me)_2$DAB$(Me)_2$}$PdCl_2$ (9300) as shown in Figure 20.

Part 1 -- Lithiation of Crosslinked Polystyrene Beads.

Following the procedure of Frechet *et al* (see above), a dry, thick-walled glass reaction bomb was charged with 1.00 g (9.60 mmol equivalents of arene)

of 100-200 mesh 1% crosslinked polystyrene beads (Advanced Chemtech) and the contents were purged with N_2(g). The resin was then suspended with 10.0 mL of dry cyclohexane and treated with 7.5 mL (12 mmol) of a 1.6 M solution of n-BuLi in hexanes and then 1.50 mL (9.9 mmol) of TMEDA. Upon addition of the TMEDA the supernatant became orange in color. The reaction mixture was then allowed to stir overnight at 65° C under N_2(g). After 15 h of heating the supernatant was removed from the reddish colored resin and the resin was washed with fresh, dry cyclohexane 3 x 7 mL, allowing it to stir in the cylcohexane for 5 min with each addition of the solvent before tranferring away the supernatant. After the final rinse, the resin was charged with 5.0 mL of fresh cyclohexane and used for the graft polymerization syntheses described in Part 2 and Part 3 below.

Part 2 -- Graft Polymerization of Butadiene with Lithiated Polystyrene: PS-PBD.

To a suspension of the lithiated polystyrene resin prepared as described above was added (at 25 °C) a solution containing approximately 5 mL of butadiene (90 mmol) that had been previously condensed into 10 mL of cyclohexane. The reaction mixture was slowly stirred under N_2(g) behind a blast shield and after 10 min there was an immediate exothermic reaction that caused the contents of the bomb to boil and become hot to the touch. The bomb was placed in a bath of ice water and after a few minutes an additional 5.0 mL of cyclohexane was added. After the flask had cooled it was removed from the ice bath and allowed to continue stirring at room temperature. The volume of the resin had noticeably increased and after 2 h of total reaction time the reaction mixture was quenched with 20-30 mL of methanol and the colorless beads were collected over a glass frit. The beads were then washed with THF (2 x 10 mL) and the alternatively with THF and H_2O (3 x 30 mL each). After a final wash with 30 mL of THF they were transferred to a tared vial and dried overnight in vacuo. Isolated Yield: 2.38 g of colorless beads. A lower limit of the loading of diene ligand was calculated to be 6.5 mmol/g, based on the weight gain in the resin.

Part 3 -- Graft Polymerization of Isoprene with Lithiated Polystyrene: PS-PI.

To a suspension of the lithiated polystyrene resin in 20 mL of cyclohexane prepared as described above was added approximately 5 mL (70 mmol) of isoprene. The reaction mixture was slowly stirred behind a blast shield while heating under an N_2(g) atmosphere at 50-55 °C for 14 h. Upon completion of the reaction the volume of the resin had increased significantly. The milky reaction mixture was quenched with 30-40 mL of methanol and the colorless beads were collected over a glass frit. The beads were then washed with toluene (5 x 20 mL) and then with THF (5 x 20 mL). After drying the resin overnight in vacuo the odor of THF could still be detected and so the solids were washed with diethyl ether (10 x 10 mL), allowing a few minutes of contact between the solvent and the solids with each wash before filtering. The solids were collected and dried overnight in vacuo. Isolated Yield: 2.01 g of colorless beads. A lower limit of the loading of diene ligand was calculated to be 7.4 mmol/g, based on the weight gain in the resin.

Part 4 -- Preparation of PS-PBD-{$PdCl_2$}.

A glass scintillation vial was charged with PS-PBD (200 mg, 1.3 mmol equivalents of diene ligand) and was then treated with a solution containing $(PhCN)_2PdCl_2$ (200 mg, 0.52 mmol) in 12 mL of toluene. The suspension was agitated on an orbital shaker at 25 °C for 4.5 h during which time the resin had become dark amber and the color of the supernatant had bleached significantly. The supernatant was transferred away from the resin with a pasteur pipette and washed with toluene (10 x 3 mL) allowing 5 min of contact time between the solvent and resin before removing the supernatant each time. The resin was then filtered and further washed with toluene (8 x 2-3 mL) and dried overnight. The dried resin was suspended in 4 mL of CH_2Cl_2 in a vial for a couple hours to allow any insoluble inorganic materials to settle out. Some reddish solids, possibly $PdCl_2$, were removed from the bottom of the vial and the resin was again suspended in CH_2Cl_2 to ensure that all the solids had been removed. The resin was finally washed with CH_2Cl_2 (5 x 2 mL) and dried overnight in vacuo. Loading of the brick-red colored resin (based on Pd analysis): 1.6 mmol/g (9.27% Pd).

Part 5 -- Preparation of PS-PI-{$PdCl_2$}.

A glass scintillation vial was charged with PS-PI (200 mg, 1.48 mmol equivalents of diene ligand) and treated with a solution containing $(PhCN)_2PdCl_2$ (200 mg, 0.52 mmol) in 10 mL of toluene. The suspension was stirred on an orbital shaker at 25 °C for 20.5 h during which time the resin had become dark red amber in color and the supernatant had lost much of its color. The resin was worked up as described in Part 4 of Example 1, above. After drying in vacuo overnight a brick-red colored solid was obtained and analyzed for Pd. Loading (based on Pd): 1.58 mmol/g (16.78% Pd).

Part 6 -- Preparation of PS-PBD-{PdMeCl}.

In a glass scintillation vial was placed PS-PBD (200 mg, 1.3 mmol equivalents of diene ligand) followed by a solution containing (COD)PdMeCl (200 mg, 0.76 mmol) in 11 mL of toluene. The suspension was stirred for 3 h on an orbital shaker during which time the resin began appear a light yellow in color and eventually became a yellow brown color. The supernatant was removed from the resin with a pasteur pipette and was washed as described in Part 4 of Example 1, above. The washed resin was then dried overnight in vacuo and analyzed for Pd. Loading (based on Pd analysis): 0.86 mmol/g (9.15% Pd).

Part 7 -- Preparation of PS-PI-{PdMeCl}.

In a glass scintillation vial was placed PS-PI (100 mg, 0.74 mmol) followed by a solution containing (COD)PdMeCl (50 mg, 0.19 mmol) in 4 mL of toluene. The suspension was allowed to stir on a orbital shaker for 21.5 h after which time the resin had become yellow in color. The resin was worked up as described in Part 4 of Example 1, above. The yellow resin was then dried overnight in vacuo and analyzed for palladium. Loading (based on Pd): 0.214 mmol/g (2.28% Pd).

Part 8 -- Reaction of PS-PBD-{$PdCl_2$} with $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$.

In a glass vial was placed PS-PBD-{$PdCl_2$} (36 mg, 0.031 mmol) followed by a solution containing 5.0 mL (0.016 mmol equivalents of diazabutadiene

chelating ligand) of $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$ in 1.0 mL of dry CD_2Cl_2. The suspension was allowed to react at 25 °C by agitating with an orbital shaker and the progress of the reaction was monitored by ^1H NMR. After 1 h the NMR showed significant loss of resonances attributed to free diazabutadiene ligand and the appearance of new resonances corresponding to the product $\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}PdCl_2$. The precipitation of a crystalline yellow solid was also observed, consistent with the formation of the sparingly soluble product. After 1 day of reaction the NMR showed only resonances for the product, there were more yellow solids in the supernatant, and the color of the resin had faded substantially to a yellow-orange.

Part 9 -- Reaction of PS-PI-$\{PdCl_2\}$ with $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$.

This reaction was done analogously to that done in above in part 8 of Example 2 with the exception that PS-PI-$\{PdCl_2\}$ was used (20 mg, 0.031 mmol), and the reaction proceeded in essentially the same manner with similar observations as those described above.

EXAMPLE 3

This example illustrates the utility of Merrifield resin as a scaffold from which ligating groups such as *N,N,N'*-trimethylethylenediamine can be attached (as shown in Figure 21). Crosslinked chloromethylated polystyrene beads (9400) can be treated with *N,N,N'*-trimethylethylenediamine (9500) resulting in the formation of a solid supported chelating {2,0} diamine ligand, PS-TMEDA (9600), that can mimic the ligation of TMEDA. The PS-TMEDA resin (9600) can then be reacted with with $(PhCN)_2PdCl_2$ or (COD)PdMeCl (by way of substitution of the PhCN or COD ligands respectively) resulting in the formation of the solid supported $\{PdCl_2\}$ and {PdMeCl} species, PS-TMEDA-$\{PdCl_2\}$ (L = Cl: 9700) and PS-TMEDA-{PdMeCl} (L= Me: 9800). Other partially ligated metal complexes can also be scavenged by PS-TMEDA as is demonstrated below.

Part 1 -- Preparation of PS-TMEDA.

A 100 mL round bottom flask was loaded with chloromethylated polystyrene beads (Merrifield Resin, 1.12 mmol/g loading, based on Cl) followed by 50 mL of dry DMF. The suspension was treated with *N,N,N'*-trimethylethylenediamine (5.27 g, 0.56 mol, 10 equivalents) and the reaction mixture was heated between 65-75 °C for 16 h and then at 75 °C for 8 h. The reaction was allowed to cool to room temperature and the contents were filtered and washed as follows: DMF (2 x 30 mL), 4:1 THF/H_2O/half sat'd $NaHCO_3$(aq) (4 x 30 mL), 4:1 THF/H_2O (3 x 30 mL), THF (3 x 30 mL), H_2O (3 x 30 mL), DMF (30 mL), THF (3 x 30 mL), and diethyl ether (3 x 30 mL). With each washing the solids were allowed 5 min contact time with the solvent(s) before filtering. The solids were then dried overnight in vacuo yielding 4.92 g of off-white colored beads.

Part 2 -- Preparation of PS-TMEDA-{$PdCl_2$}.

In a glass scintillation vial was placed PS-TMEDA (100 mg, 0.093 mmol of chelating ligand) followed by a solution containing $(PhCN)_2PdCl_2$ (50 mg, 0.13 mmol) in 4 mL of toluene. The suspension was stirred on an orbital shaker for 21 h at which point the resin had become red in color and the supernatant was essentially clear. The resin was worked up as described in Part 4 of Example 1 (above) and was dried overnight in vacuo. Loading (based on Pd): 0.93 mmol/g (9.88% Pd).

Part 3 -- Preparation of PS-TMEDA-{PdMeCl}.

In a glass scintillation vial was placed PS-TMEDA (100 mg, 0.093 mmol of chelating ligand) followed by a solution containing $(PhCN)_2PdCl_2$ (50 mg, 0.13 mmol) in 4 mL of toluene. The suspension was stirred on an orbital shaker for 21 h at which point the resin had become yellow in color. The resin was worked up as described in Part 4 of Example 1 (above) and was dried overnight in vacuo. Loading (based on Pd): 0.73 mmol/g (7.71% Pd).

Part 4 -- Preparation of PS-TMEDA-{MgMeCl}.

To a suspension 0.100 g of PS-TMEDA in 3.5 mL of THF was added 333 μL (0.999 mmol) of a 3M solution of MgMeCl in THF and the reaction mixture was shaken for 24 h under N_2(g). The suspension was filtered over a coarse glass frit and washed with THF (5 x 10 mL) and diethyl ether (5 x 10 mL) and was dried in vacuo for 24 h. Yield of white resin: 0.097 g. Loading (based on Mg): 1.24 mmol/g (3.02% Mg).

Part 5 -- Preparation of PS-TMEDA-{ZnMeCl}.

To a suspension 0.100 g of PS-TMEDA in 3.5 mL of CH_2Cl_2 was added 500 μL (1.0 mmol) of a 2M solution of ZnMeCl in THF and the reaction mixture was shaken for 24 h under N_2(g). The suspension was filtered over a coarse glass frit and washed with THF (5 x 10 mL) and diethyl ether (5 x 10 mL) and was dried in vacuo for 24 h. Yield of white resin: 0.115 g. Loading (based on Zn): 1.24 mmol/g (8.10% Zn).

Part 6 -- Preparation of PS-TMEDA-{$ZnMe_2$}.

To a suspension 0.100 g of PS-TMEDA in 3.5 mL of CH_2Cl_2 was added 333 μL (0.333 mmol) of a 1M solution of $ZnMe_2$ in heptane and the reaction mixture was shaken for 24 h under N_2(g). The suspension was filtered over a coarse glass frit and washed with THF (5 x 10 mL) and pentane (5 x 10 mL) and was dried in vacuo for 24 h. Yield of white resin: 0.115 g. Loading (based on Zn): 1.12 mmol/g (7.30% Zn).

EXAMPLE 4

Crosslinked polystyrene functionalized with the polystyrene supported tetraamine ligand tris-(2-aminoethyl)-amine (Polyamine resin HL™, 200-400 mesh) and often used in resin based organic synthesis. This tetraamine functionality is also used in its soluble form ($(H_2NCH_2CH_2)_3NH$, abbreviated as TREN) as a metal chelating agent because of the three pendant, potentially coordinating amines. Treatment of the polystyrene bound TREN resin ((PS-TREN, 9900) with $(PhCN)_2PdCl_2$ or (COD)PdMeCl (by way of substitution of PhCN or COD

respectively) results in the formation of the solid supported {$PdCl_2$} and {PdMeCl} species, PS-TREN-{$PdCl_2$} (L = Cl: 10000) and PS-TREN-{PdMeCl} (L = Me: 10100) as shown in Figure 22.

Part 1 -- Preparation of PS-TREN-{$PdCl_2$}.

In a glass scintillation vial was placed PS-TREN (100 mg, 0.40 mmol of chelating primary amine ligands) followed by a solution containing $(PhCN)_2PdCl_2$ (50 mg, 0.13 mmol) in 4 mL of toluene. The suspension was stirred on an orbital shaker for 20.5 h at which point the resin had become red in color and the supernatant was essentially clear. The resin was worked up as described in Part 4 of Example 1 (above) and was dried overnight in vacuo. Loading (based on Pd): 0.97 mmol/g (10.27% Pd).

Part 2 -- Preparation of PS-TREN-{PdMeCl}.

In a glass scintillation vial was placed PS-TREN (100 mg, 0.40 mmol of chelating primary amine ligands) followed by a solution containing (COD)PdMeCl (50 mg, 0.19 mmol) in 4 mL of toluene. The suspension was stirred on an orbital shaker for 20.5 h at which point the resin had become yellow in color. The resin was worked up as described in Part 4 of Example 1 (above) and was dried overnight in vacuo. Loading (based on Pd): 1.04 mmol/g (11.11% Pd).

EXAMPLE 5

Part 1 -- Preparation of PS-N-Methylpiperazine

0.5 g of Merrifield resin (loading 4.3 mmol/g, 2.15 mmol) was treated with 2.15 g N-methylpiperazine (21.5 mmol) in 100 mL THF and refluxed overnight. The resultant resin was then collected by filtration and washed with 2 x 50 mL THF, CH_2Cl_2, EtOH, CH_2Cl_2, EtOH, CH_2Cl_2 and dried under vacuum to produce white beads of PS-N-Methylpiperazine. Loading based on nitrogen: 3.1 mmol/g (8.69 % N).

Part 2 -- Preparation of PS-N-Phenylpiperazine

2.0 g of Merrifield resin (loading 4.3 mmol/g, 8.60 mmol) was treated with 3.63 g N-phenylpiperazine (22.4 mmol) in THF and refluxed overnight. The resultant resin was then collected by filtration and washed with THF, EtOH, CH_2Cl_2 and dried under vacuum to produce white beads of PS-N-phenylpiperazine. Loading based on nitrogen: 1.4 mmol/g (3.87 % N).

Part 3 -- Preparation of PS-N-Methylpiperazine-{PdMeCl}

0.5 g of PS-N-Methylpiperazine was treated with a solution of (COD)PdMeCl (0.8 g 3.0 mmol) in 20 mL CH_2Cl_2. After agitating the solution for 3 hours, the resultant orange-yellow resin was collected by fitration, and washed with 60 mL CH_2Cl_2, 60 mL toluene, 30 mL pentane and dried in vacuum. Loading (based on Pd): 0.4 mmol/g (4.68 % Pd).

Part 4 -- Preparation of PS-N-Methylpiperazine-{$AlMe_3$}

0.4 g of PS-N-Methylpiperazine was treated with a solution of $AlMe_3$ (5 mL, 2 M solution in hexanes) in 20 mL toluene. After agitating the solution for 2 hours, the resultant white resin was collected by fitration, and washed with 60 mL toluene, 30 mL pentane and dried in vacuum.

Part 5 -- Preparation of PS-N-Phenylpiperazine-{$NiBr_2$}

0.5 g of PS-N-Phenylpiperazine was treated with a suspension of (DME)$NiBr_2$ (0.2 g, 0.6 mmol) in 20 mL CH_2Cl_2. After agitating the solution for 24 hours, the resultant green resin was collected by filtration, and washed with acetone to remove any excess (DME)$NiBr_2$, then additionally washed with 60 mL CH_2Cl_2, 60 mL toluene, 30 mL pentane and dried in vacuum. Loading (based on Ni) : 0.9 mmol/g (5.59 % Ni).

Part 6 -- Reaction of PS-N-Methylpiperazine-{PdMeCl} with $(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$

0.10 g of PS-N-Methylpiperazine-{PdMeCl} was treated with a solution {$(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$} (0.005 g 0.016 mmol) in 10 mL CH_2Cl_2. The resultant mixture was agitated for 30 minutes producing an orange colored supernatant solution. The supernatant solution was collected by filtration and the solvent was removed under a stream of nitrogen producing {$(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2$}PdMeCl as an orange powder (0.007 g, 94 % yield).

EXAMPLE 6

Part 1 -- Preparation of PS-TMPDA.

In a 200 mL flask was placed 5 g (5.6 mmol; 1.12 mmol/g loaded, 1% crosslinked, 100-200 mesh) Merrifield resin followed by 100 mL of dry DMF. The suspension was treated with 9.8 g (0.084 mol; 15 equivalents) of *N,N,N'*-trimethyl-1,3-propanediamine and heated between 75-85 °C under N_2(g) for 21.5 h. The resin was filtered and washed with DMF (4 x 50 mL), 3:1 THF : sat'd $NaHCO_3$ (2 x 50 mL), 4:1 THF : H_2O (4 x 50 mL), H_2O (4 x 50-60 mL), THF (4 x 50-60 mL), CH_2Cl_2 (4 x 50 mL), toluene (4 x 50 mL) and diethyl ether (6 x 50 mL). The resin was then dried for approximately 1 day in vacuo yielding 4.76 g of product. Loading (based on nitrogen analysis, 2 nitrogens per unit of chelate): 0.91 mmol/g (2.54% N).

Part 2 -- Preparation of PS-TMPDA-{PdMeCl}.

In the glove box a glass scintillation vial was charged with 0.200 g (.18 mmol) of PS-TMPDA along with 0.200 g of (COD)PdMeCl (0.76 mmol; a 4.2-fold excess) and 3-4 mL of dry toluene. The suspension was shaken and within seconds the initially colorless resin began to appear yellow (the supernatant was colorless). After 4h 15 min of shaking the resin had taken on an olive green color. It was filtered over a coarse glass frit and washed with 5 x 10 mL of toluene, 5 x 10 mL of diethyl ether and was dried for 24 h in vacuo to give 0.216 g of olive green product. Loading (based on Pd): 0.84 mmol/g (8.91% Pd).

EXAMPLE 7

The following example illustrates the use of a metal delivery agent and a ligand scavenging agent in combination to prepare an array of organometallic palladium compounds that are catalyst precursors for ethylene polymerization.

Part 1 – Use of PS-TMPDA-{PdMeCl} and Amberlyst-15™ in The Synthesis of A Library of Catalyst Precursors.

An array of 6 diazabutadiene ligands, $(R_1)_2DAB(R_2)_2$ (R_1 = 2,4,6-$Me_3C_6H_2$, 2-Me, 2,6-diisopropyl; $(R_2)_2$ = $(Me)_2$, acenapthaquinone), contaminated with precursor anilines (R_1NH_2) remaining from the synthesis of the ligand library (ca. 0.05 mmol DAB and 0.05 mmol aniline in 400 µL of CH_2Cl_2) was distributed into individual wells of a 800 µL filter bottom microtiter plate. To each well was added 40 mg of PS-TMEDA-{PdMeCl} metal delivery agent, and the mixture was shaken under N_2(g) for 24 h. The reaction mixtures within the wells became yellow-orange to red-orange in color over the course of the reaction, indicating the formation of the desired metal-ligand products. To each well was then added 50 mg of Amberlyst-15™ sulfonic acid functionalized polystyrene resin, a ligand scavenging agent, and the plate was shaken for 2 h. The contents of the plate were filtered into a 1 mL microtiter receiving plate and the resins were washed with 200 µL of CH_2Cl_2. The solvent was removed from the plate to provide an array of orange to red colored complexes, $((R_1)_2DAB(R_2)_2)PdMeCl$, in yields ranging from 45-78%. The complexes were

determined to be pure by comparison of their ^{1}H NMR spectra with authentic examples.

EXAMPLE 8

Part 1 -- Preparation of A Resin Bound Non-Coordinating Anion: Poly(2,6-di-t-Bu(4-vinylpyridine))$\{HBAr'_4\}$.

In a glovebox, a slurry of poly(2,6-di-t-Bu(4-vinylpyridine)) (10.32 g) and Et_2O (200 mL) was prepared. Solid $\{H(OEt_2)_2\}\{BAr'_4\}$ (21.6 g, 21.6 mmol) was added. The mixture was shaken overnight, filtered, washed with Et_2O (3 x 150 ml), toluene (150 mL) and pentane (150 mL). The resulting off-white resin was dried in vacuo overnight. The loading level was determined by fluorine analysis. (yield 27.4 g, 95 %, loading = 0.66 mmol $HBAr'_4$/g)

Part 2 -- Use of A Resin Bound Non-Coordinating Anion as A Ligand Delivery Agent in the Preparation of $\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}Ni(CH_2SiMe_3)(CH_3CN)\}^+\{BAr'_4\}^-$.

$\{(2,4,6\text{-}Me_3C_6H_2)_2DAB(Me)_2\}Ni(CH_2SiMe_3)_2$ (35 mg, 0.063 mmol.) was dissolved in 5 mL Et_2O. CH_3CN (100 μL) was added and the solution was cooled to –35 °C and solid poly(2,6-di-t-Bu(4-vinylpyridine))$\{HBAr'_4\}$ (0.78 mmol/g, 135 mg, 0.105 mmol) was added. The mixture was shaken for 2 h at 25 °C and filtered. The resin was washed with additional Et_2O (10 mL) and the combined Et_2O fractions were combined. Et_2O was removed *in vacuo*, yielding a red microcrystalline solid that was pure by ^{1}H NMR and elemental analysis. (yield: 79 mg, 92%). Anal: Calc'd for $C_{60}H_{54}N_3BF_{24}NiSi$. C, 52.58; H, 3.97; N, 3.07. Found: c, 52.92; H, 3.95; N, 2.94.

EXAMPLE 9

Part 1 -- Preparation of PS-$ArCO_2$-$\{ZnCl(THF)\}$.

In the glove box a glass scintillation vial was charged with 0.200 g (0.35 mmol, 1.77 mmol/g loaded) of polystyrene supported carboxylic acid, PS-$ArCO_2H$ followed by 1-2 mL of dry THF. The suspension was treated with 1.83 g (3.5 mmol; a 10-fold excess) of a 2.0 M solution of MeZnCl in THF resulting in the

formation of hydrogen bubbles rising from the resin. After a 1-2 minutes of shaking the reaction mixture the bubbles had ceased and the resin was allowed to shake for 21 h. The resin was collected over a medium glass frit and was washed with 5 x 10 mL of dry THF and dried for 24 h in vacuo yielding 0.217 g of white resin. Loading (based on Zn): 1.10 mmol/g (7.17% Zn).

EXAMPLE 10

Part 1 -- Preparation of SiO_2-n-PrCN-{$PdCl_2$(PhCN)}.

To a glass scintillation vial was added 0.100 g (0.26 mmol) $(PhCN)_2PdCl_2$ followed by 3 mL of CH_2Cl_2 giving an amber colored solution. To this solution was added 0.100 g (0.18 mmol) of silica functionalized with propionitrile groups SiO_2-$CH_2CH_2CH_2CN$ (Bakerbond™ reversed phase Narrow Pore Cyano packing) and the suspension was shaken. Almost immediately the silica took on a brick red color while the supernatant became lighter in color. After 24 h the dark reddish brown silica was filtered over a frit and washed with CH_2Cl_2 (3 x 5 mL) and diethylether (3 x 5 mL) and dried for several hours in vacuo. Loading (based on Pd): 0.88 mmol/g (9.34% Pd).

Part 2 -- Preparation of SiO_2-n-PrCN-{$ReCl_3(PPh_3)_2$}.

To a glass scintillation vial was added 0.100 g (0.117 mmol) $ReCl_3(MeCN)(PPh_3)_2$ followed by 3 mL of CH_2Cl_2 giving an amber colored solution. To this solution was added 0.100 g (0.18 mmol) of silica functionalized with propionitrile groups SiO_2-$CH_2CH_2CH_2CN$ (Bakerbond™ reversed phase Narrow Pore Cyano packing) and the suspension was shaken. Almost immediately the silica took on a light orange color while the supernatant became slightly lighter in color. After 24 h the light orange silica was filtered over a frit and washed with CH_2Cl_2 (3 x 5 mL) and diethylether (3 x 5 mL) and dried for several hours in vacuo. Loading (based on Re): 0.06 mmol/g (1.13% Re).

Those of skill in the art will appreciate variations of the above that do not deviate from the scope and spirit of the invention.

CLAIMS :

1. A method of making metal-ligand compounds. the method comprising the steps of:

a) providing an array of ligands. and

b) adding a metal delivery agent to each element of said array of ligands;

wherein a metal atom or ion is detached from the metal delivery agent and said metal atom or ion binds with at least one element in the array of ligands to create a metal-ligand compound.

2. The method of claim 1 further comprising the step of separating any unreacted metal by filtration.

3. The method of claim 1. wherein the metal delivery agent comprises a solid support and the metal bonded to the solid support. the metal is detached from the solid support.

4. The method of claim 3, wherein the metal delivery agent additionally comprises a tether disposed between the metal and the solid support,

wherein the metal is bonded to the tether at a first site on the tether and the solid support is bonded to the tether at a second site on the tether, and

wherein the metal is detached from the tether.

5. The method of claim 4, wherein the metal delivery agent additionally comprises a leaving group ligand disposed between the tether and the metal,

wherein the leaving group ligand is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group,

and wherein the metal is detached from the leaving group ligand.

6. The method of claim 3, wherein the metal is chosen from the group consisting of Groups 1-15 of the Periodic Table of Elements.

7. The method of claim 3, wherein the metal is a partially or fully ligated metal.

8. The method of claim 7, wherein the partially or fully ligated metal comprises one or more ligands selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

9. The method of claim 8, wherein the one or more ligands on the partially or fully ligated metal is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

10. The method of claim 5, wherein the metal delivery agent is selected from the group consisting of PS-PEG-OMe-{$NiBr_2$}, PS-PEG-OMe-{$PdCl_2$}, PS-PEG-OMe-{$CoCl_2$}, PS-PEG-OMe-{VCl_3}, PS-PEG-OMe-{$ZnCl_2$}, PS-PEG-OMe-{$FeCl_2$}, PS-PBD-{$PdCl_2$}, PS-PBD-{PdMeCl}, PS-PI-{$PdCl_2$}, PS-PI-{PdMeCl}, PS-TMEDA-{$PdCl_2$}, PS-TMEDA-{PdMeCl}, PS-TMEDA-{MgMeCl}, PS-TMEDA-{$ZnMe_2$}, PS-TMEDA-{ZnMeCl}, PS-TREN-{$PdCl_2$}, PS-TREN-{PdMeCl}, PS-N-Methylpiperazine-{PdMeCl}, PS-N-Methylpiperazine-{$AlMe_3$}, PS-N-Phenylpiperazine-{$NiBr_2$}, PS-TMPDA-{PdMeCl}, PS-PEG-OMe-{$TiCl_4$}, PS-PEG-OMe-{$HfCl_4$}, PS-PEG-OMe-{$MoCl_3$}, PS-PEG-OMe-{$NbCl_3$}, PS-PEG-Br{Ta(=N(2,4,6-$(CH_3)_3C_6H_2$))Cl_3}, PS-ArCO_2-{ZnCl(THF)},

SiO_2-n-PrCN-{$PdCl_2(PhCN)$}, and SiO_2-n-PrCN-{$ReCl_3(PPh_3)_2$}.

11. The method of claim 3, wherein the solid support is selected from the group consisting of organic polymers, inorganic solids, and dendrimeric materials.

12. The method of claim 5, wherein the leaving group ligand is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls and combinations thereof.

13. The method of claim 12 wherein the leaving group ligand is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-Methylpiperazine, N-phenylpiperazine, TMPDA, nitriles and carboxylates.

14. The method of claim 1, wherein the array of ligands comprises at least 10 ligands at discrete locations.

15. The method of claim 14, wherein the array of ligands comprises at least 100 ligands.

16. The method of claim 15, wherein the array of ligands comprises at least 1000 ligands.

17. The method of claim 16, wherein the array of ligands comprises at least 10,000 ligands.

18. The methods of either of claims 1, 14, 15, 16 or 17, wherein each ligand within the ligand array is chosen, independently, from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

19. The method of claim 18, wherein each ligand within the ligand array is selected, independently, from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

20. The method of claim 4 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the leaving group ligand or solid support.

21. The method of claim 1, wherein an array of metal-ligand compounds is formed and said array comprises at least 10 compounds.

22. The method of claim 21, wherein the array of metal-ligand compounds comprises at least 100 compounds.

23. The method of claim 22, wherein the array of metal-ligand compounds comprises at least 1000 compounds.

24. The method of claim 23, wherein the array of metal-ligand compounds comprises at least 10.000 compounds.

25. The method of either of claims 21, 22, 23 or 24, wherein each metal-ligand compound is at a discrete location on a substrate.

26. The method of claim 1 wherein the ligand array is disposed in a solution to which the metal delivery agent is added such that the metal-ligand compound is formed in said solution.

27. A method of making metal-ligand compounds, the method comprising the steps of:

a) providing an array of metal precursors;

b) adding a ligand delivery agent to each element of the array of metal precursors; and

wherein a ligand is detached from the ligand delivery agent and said ligand binds with at least one element in the array of metal precursors to create a metal-ligand compound.

28. The method of claim 27, additionally comprising the step of separating any excess ligand delivery agent from the metal-ligand compound by filtration.

29. The method of claim 27, wherein the ligand delivery agent comprises a solid support and the ligand bonded to the solid support and the ligand is detached from the solid support.

30. The method of claim 27, wherein the ligand delivery agent additionally comprises a tether disposed between the ligand and the solid support, wherein the ligand is bonded to the tether at a first site on the tether and the solid support is bonded to the tether at a second site on the tether, and

wherein the ligand is detached from the tether.

31. The method of claim 28, wherein the ligand delivery agent additionally comprises a ligating group and a metal disposed between the tether and the ligand,

wherein the ligating group is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group,

and wherein the metal atom is bonded to the ligating group at one site on the metal atom and bonded to the ligand at a second site on the metal atom,

and the ligand is detached from the metal.

32. The method of claim 31, wherein the metal is chosen from the group consisting of Group 1-15 of the Periodic Table of Elements.

33. The method of claim 31, wherein the metal is a partially or fully ligated metal.

34. The method of claim 33, wherein the partially or fully ligated metal comprises one or more ligands selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

35. The method of claim 34, wherein the one or more ligands on the partially or fully ligated metal is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates,

thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

36. The method of claim 29, wherein the solid support is selected from the group consisting of organic polymers, inorganic solids, and dendrimeric materials.

37. The method of claim 31, wherein the ligating group is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls and combinations thereof.

38. The method of claim 37 wherein the ligating group is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-methylpiperazine, N-phenylpiperazine, poly(2,6-di-t-Bu(4-vinylpyridine)), TMPDA, nitriles and carboxylates.

39. The method of claim 27, wherein the array of metal precursors comprises at least 10 metals at discrete locations.

40. The method of claim 39, wherein the array of metal precursors comprises at least 100 metals.

41. The method of claim 40, wherein the array of metal precursors comprises at least 100 metals.

42. The method of claim 41, wherein the array of metals comprises at least 10,000 metals.

43. The methods of either of claims 27, 40, 41, 41 or 43, wherein each metal precursor in the array of metal precursors is, independently, selected from the group of Group 1-15 of the Periodic Table of Elements.

44. The method of claim 27, wherein the ligand being delivered from the ligand delivery agent is selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

45. The method of claim 44, wherein the ligand being delivered is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

46. The method of claim 30 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the leaving group ligand or solid support.

47. The method of claim 27, wherein an array of metal-ligand compounds is formed and said array comprises at least 10 compounds.

48. The method of claim 42, wherein the array of metal-ligand compounds comprises at least 100 compounds.

49. The method of claim 47, wherein the array of metal-ligand compounds comprises at least 1000 compounds.

50. The method of either of claims 46, 47 or 48, wherein each metal-ligand compound is at a discrete location on a substrate.

51. The method of claim 27 wherein the metal precursor array is disposed in a solution to which the ligand delivery agent is added such that the metal-ligand compound is formed in said solution.

52. The method of claim 31 wherein the ligand delivery agent is selected from the group consisting of PS-TMEDA-{MgMeCl}, PS-TMEDA-{ZnMeCl}, PS-TMEDA-{$ZnMe_2$}, PS-N-Methylpiperazine-{$AlMe_3$}, and Poly(2,6-di-t-Butyl(4-vinylpyridine)){$HBAr'_4$}.

53. A method of making organometallic compounds, comprising the steps of:

a) providing an array of ligands;

b) adding at least one metal precursor to each element of the ligand array; and

c) adding a scavenging agent to each element of the ligand array with the scavenging agent selected from the group consisting of metal scavenging agents, ligand scavenging agents and combinations thereof;

and wherein at least one ligand in the ligand array and at least one metal precursor bind together.

54. The method of claim 53 additionally comprising the step of filtering off the scavenging agent.

55. The method of claim 53, wherein the metal scavenging agent comprises a solid support and a ligating group which binds the metal precursor during the scavenging step.

56. The method of claim 55, wherein the metal scavenging agent additionally comprises a tether disposed between the ligating group and the solid support,

wherein the ligating group is bonded to the tether at a first site on the tether and the tether is bonded to the solid support at a second site on the tether.

57. The method of claim 56, wherein the ligating group is selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

58. The method of claim 57, wherein the ligating group is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

59. The method of claim 58 wherein the ligating group is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-Methylpiperazine, N-phenylpiperazine, poly(2,6-di-t-Bu(4-vinylpyridine)), TMPDA, nitriles and carboxylates.

60. The method of claim 55, wherein the solid support is selected from the group consisting of organic polymers, inorganic solids, and dendrimeric materials.

61. The method of claim 53, wherein the array of ligands comprises at least 10 ligands at discrete locations.

62. The method of claim 61, wherein the array of ligands comprises at least 100 ligands.

63. The method of claim 62, wherein the array of ligands comprises at least 1000 ligands.

64. The method of claim 63, wherein the array of ligands comprises at least 10,000 ligands.

65. The methods of either of claims 53, 61, 62, 63 or 64, wherein each ligand within the ligand array is selected, independently, from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

66. The method of claim 65, wherein each ligand within the ligand array is selected, independently, from the group consisting of amines, imines, amides,

imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

67. The method of claim 56 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the ligating group or solid support.

68. The method of claim 53, wherein an array of organometallic compounds is formed, which comprises at least 10 compounds.

69. The method of claim 68, wherein the array of organometallic compounds comprises at least 100 compounds.

70. The method of claim 69, wherein the array of organometallic compounds comprises at least 1000 compounds.

71. The method of claim 70, wherein the array of organometallic compounds comprises at least 10,000 different compounds.

72. The method of either of claims 53, 68, 69, 70 or 71, wherein each organometallic compound is at a discrete location on a substrate.

73. The method of claim 53, wherein the ligand scavenging agent comprises a solid support and a vacant or reactive site to bind the excess ligand.

74. The method of claim 73, wherein the ligand scavenging agent additionally comprises a tether, a ligating group and a metal disposed between the vacant or reactive site and the solid support,

wherein the solid support is bonded to the tether at a first site on the tether and the tether is bonded to the ligating group on a second site on the tether and a first site on the ligating group,

wherein the ligating group is bonded to the metal at a second site on the ligating group, and

wherein the metal includes the vacant or reactive site.

75. The method of claim 74, wherein the metal in the ligand scavenging agent is chosen from the group consisting of Groups 1-15 of the Periodic Table of Elements.

76. The method of claim 74, wherein the metal in the ligand scavenging agent is a partially or fully ligated metal.

77. The method of claim 76, wherein the partially or fully ligated metal contains one or more ligands, which are, independently, selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

78. The method of claim 77, wherein said one or more ligands on the partially or fully ligated metal is, independently, selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl,

carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

79. The method of claim 74, wherein the solid support is selected from the group consisting of organic polymers, inorganic solids, and dendrimeric materials.

80. The method of claim 74, wherein the ligating group is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls and combinations thereof.

81. The method of claim 80 wherein the ligating group is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-Methylpiperazine, N-phenylpiperazine, poly(4-vinylpyridine), TMPDA, nitriles and carboxylates.

82. The method of claim 74 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the leaving group ligand or solid support.

83. The method of claim 53 wherein in the array of ligands, each element of said array is selected, independently, from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three

site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

84. The method of claim 83, wherein each element is, independently, selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

85. A method of making organometallic compounds, comprising the steps of:

a) providing an array of metal precursors;

b) adding at least one ligand precursor to each element of the metal precursor array; and

c) adding a scavenging agent to each element of the metal precursor array with the scavenging agent selected from the group consisting of metal scavenging agents, ligand scavenging agents and combinations thereof;

and wherein at least one metal precursor in the metal precursor array and at least one ligand precursor bind together.

86. The method of claim 85, additionally comprising the step of filtering off the scavenging agent from the organometallic compound.

87. A metal delivery agent comprising a solid support and a metal bonded to the solid support, wherein the metal is detached from the solid support and delivered into a solution during a chemical reaction.

88. The metal delivery agent claim 87, additionally comprising a tether disposed between the metal and the solid support,

wherein the metal is bonded to the tether at a first site on the tether and the solid support is bonded to the tether at a second site on the tether. and

wherein during the reaction, the metal is detached from the tether.

89. The metal delivery agent of claim 88, additionally comprising a leaving group ligand disposed between the tether and the metal,

wherein the leaving group ligand is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group.

and wherein during the reaction. the metal is detached from the leaving group ligand.

90. The metal delivery agent of claim 89. wherein the metal is chosen from the group consisting of Group 1-15 of the Periodic Table of Elements.

91. The metal delivery agent of claim 90, wherein the metal is a partially or fully ligated metal.

92. The metal delivery agent of claim 91, wherein the partially or fully ligated metal comprises one or more ligands selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

93. The metal delivery agent of claim 92, wherein the one or more ligands on the partially or fully ligated metal is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides,

acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

94. The metal delivery agent of claim 93, which is selected from the group consisting of PS-PEG-OMe-{$NiBr_2$}, PS-PEG-OMe-{$PdCl_2$}, PS-PEG-OMe-{$CoCl_2$}, PS-PEG-OMe-{VCl_3}, PS-PEG-OMe-{$ZnCl_2$}, PS-PEG-OMe-{$FeCl_2$}, PS-PBD-{$PdCl_2$}, PS-PBD-{PdMeCl}, PS-PI-{$PdCl_2$}, PS-PI-{PdMeCl}, PS-TMEDA-{$PdCl_2$}, PS-TMEDA-{PdMeCl}, PS-TMEDA-{MgMeCl}, PS-TMEDA-{$ZnMe_2$}, PS-TMEDA-{ZnMeCl}, PS-TREN-{$PdCl_2$}, PS-TREN-{PdMeCl}, PS-N-Methylpiperazine-{PdMeCl}, PS-N-Methylpiperazine-{$AlMe_3$}, PS-N-Phenylpiperazine-{$NiBr_2$}, PS-TMPDA-{PdMeCl}, PS-PEG-OMe-{$TiCl_4$}, PS-PEG-OMe-{$HfCl_4$}, PS-PEG-OMe-{$MoCl_3$}, PS-PEG-OMe-{$NbCl_3$}, PS-PEG-Br{$Ta(=N(2,4,6\text{-}(CH_3)_3C_6H_2))Cl_3$}, PS-$ArCO_2$-{ZnCl(THF)}, SiO_2-n-PrCN-{$PdCl_2(PhCN)$}, and SiO_2-n-PrCN-{$ReCl_3(PPh_3)_2$}.

95. The metal delivery agent of claim 87, wherein the solid support is selected from the group consisting of organic polymers, inorganic solids, and dendrimeric materials.

96. The metal delivery agent of claim 89, wherein the leaving group ligand is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls and combinations thereof.

97. The metal delivery agent of claim 96 wherein the leaving group ligand is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-Methylpiperazine, N-phenylpiperazine, TMPDA, nitriles and carboxylates.

98. The metal delivery agent of claim 88 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the leaving group ligand or solid support.

99. A ligand delivery agent comprising a solid support and a ligand bonded to the solid support, wherein the ligand is detached from the solid support and delivered into a solution during a chemical reaction.

100. The ligand delivery agent of claim 99, additionally comprising a tether disposed between the ligand and the solid support,

wherein the ligand is bonded to the tether at a first site on the tether and the solid support is attached to the tether at a second site on the tether and

wherein the ligand is detached from the tether and delivered into a solution during a chemical reaction.

101. The ligand delivery agent of claim 100,

additionally comprising a ligating group and a metal disposed between the ligand and the tether,

wherein the ligating group is bonded to the tether at one site on the ligating group and bonded to the metal at a second site on the ligating group,

and wherein the metal atom is bonded to the ligating group at one site on the metal and bonded to the ligand at a second site on the metal atom,

and wherein the ligand is detached from the metal and delivered into a solution during a chemical reaction.

102. The ligand delivery agent of claim 99, wherein the ligand being delivered is selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

103. The ligand delivery agent of claim 102, wherein ligand being delivered is selected from the group consisting of amines. imines, amides, imides, ethers, alkoxides, aryloxides, ketones. oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

104. The ligand delivery agent of claim 99, wherein the solid support organic polymers, inorganic solids, and dendrimeric materials.

105. The ligand delivery agent of claim 101, wherein the ligating group is selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes, carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls and combinations thereof.

106. The ligand delivery agent of claim 105 wherein the ligating group is selected from the group consisting of PEG-OMe, PEG-Br, PBD, PI, TMEDA, TREN, N-Methylpiperazine, N-phenylpiperazine, poly(2,6-di-t-Bu(4-vinylpyridine)), TMPDA, nitriles and carboxylates.

107. The ligand delivery agent of claim 101 wherein the tether is selected from the group consisting of organic molecules, inorganic molecules, partially or fully ligated metal complexes or fragments thereof and natural extensions of the leaving group ligand or solid support.

108. The ligand delivery agent of claim 101, wherein the metal is chosen from the group consisting of Group 1-15 of the Periodic Table of Elements.

109. The ligand delivery agent of claim 101, wherein the metal is a partially or fully ligated metal.

110. The method of claim 109, wherein the partially or fully ligated metal contains one or more ligands, which are, independently, selected from the group consisting of one-site, monoanionic ligands; two-site, dianionic ligands; two site, monoanionic ligands; two site, neutral ligands; three site, neutral ligands; three site, monoanionic ligands; three site, dianionic ligands; three site, trianionic ligands; four site, neutral ligands; four site, monoanionic ligands; four site, dianionic ligands; and ligands where the charge is greater than the number of sites it occupies.

111. The method of claim 110, wherein said one or more ligands on the partially or fully ligated metal is, independently, selected from the group consisting of amines, imines, amides, imides, ethers, alkoxides, aryloxides, ketones, oxides, acetates, thioethers, sulfides, phosphines, phosphides, phospha(alkenes), phosphine oxides, phosphites, aminomethylphosphines, arsines, amidines, nitriles, isonitriles, allyls, cyclopentadienyl, substituted cyclopentadienyl, indenyl, fluorenyl, carboxylates, thiolates, alkyls, substituted alkyls, aryls, substituted aryls, carbenes,

carbynes, alkenes, alkynes, sulfates, sulfonamides, silyls, halogens and combinations thereof.

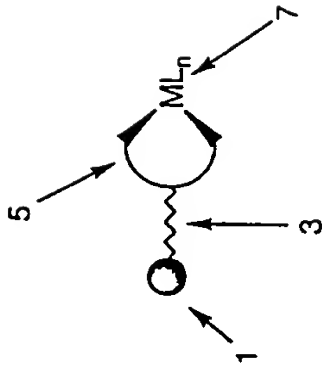


Figure 1

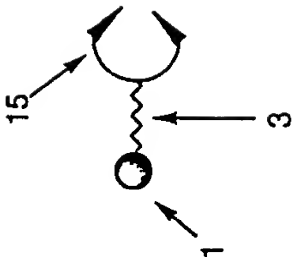


Figure 2

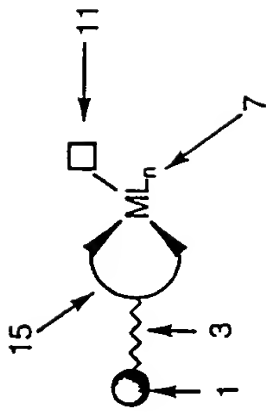


Figure 3

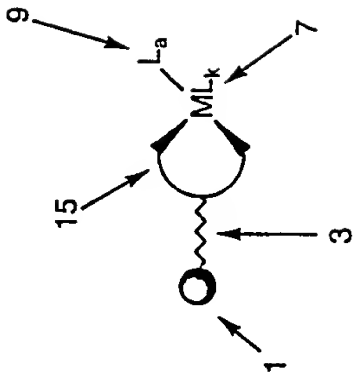
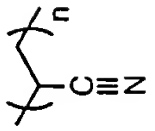
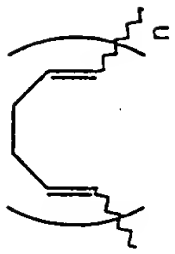


Figure 4



6000

Figure 5b

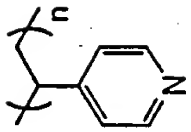


6200

Figure 5d

5900

Figure 5a



6100

Figure 5c

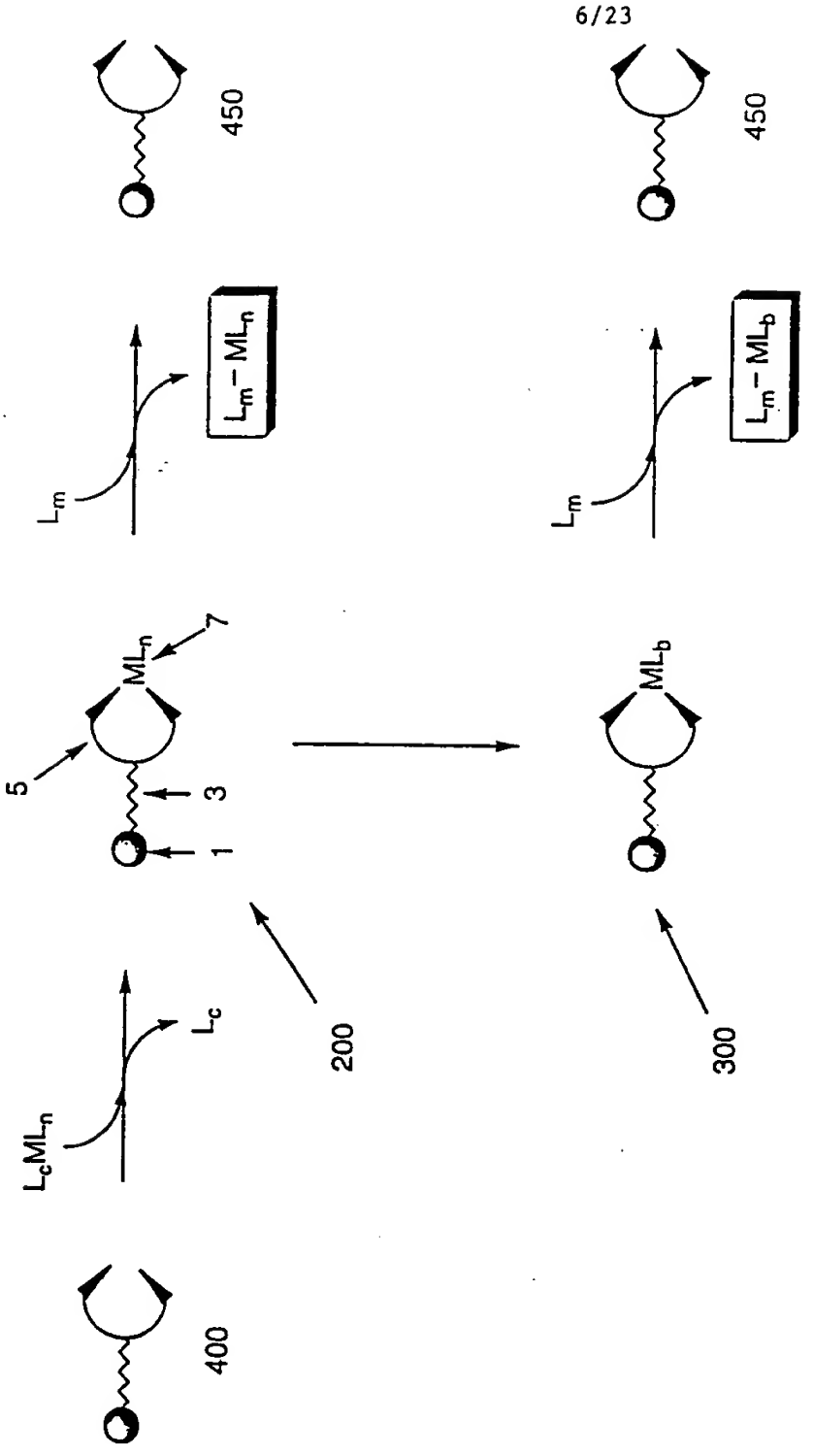


Figure 6

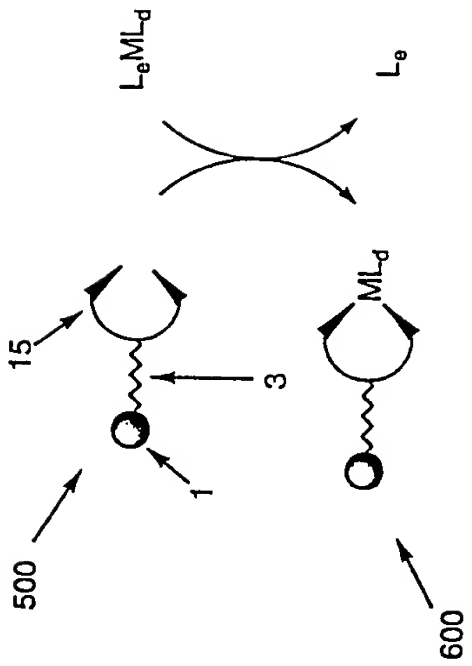


Figure 7

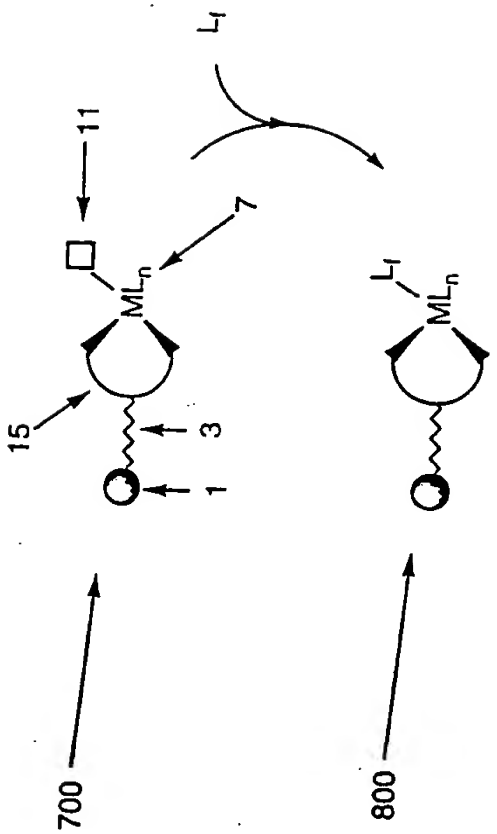


Figure 8

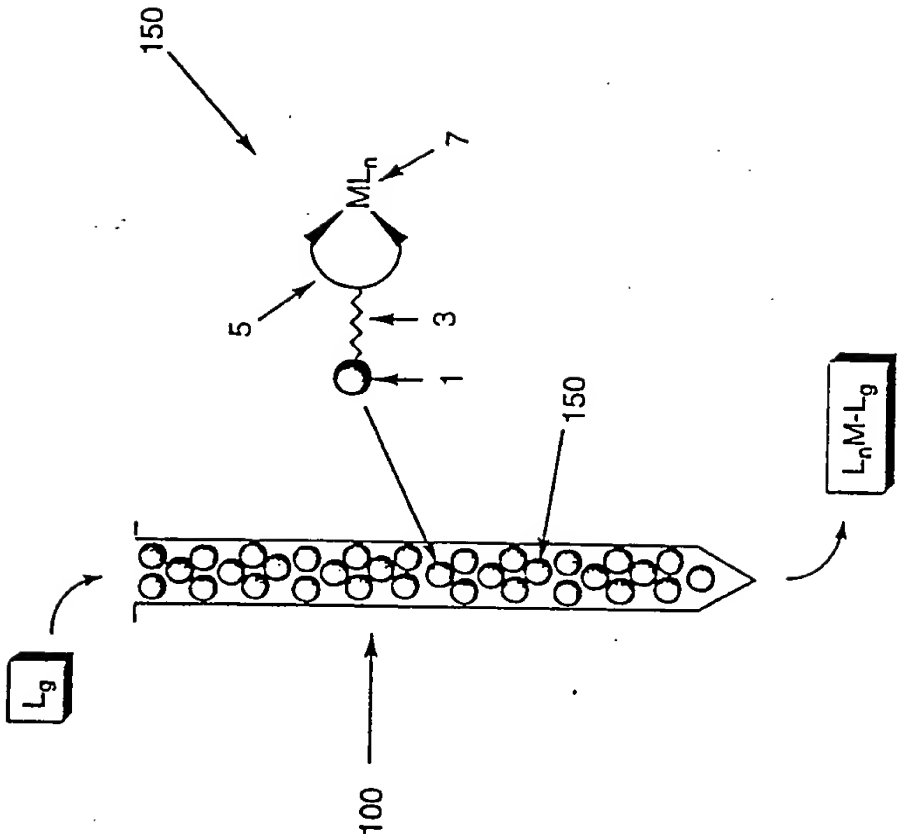


Figure 9

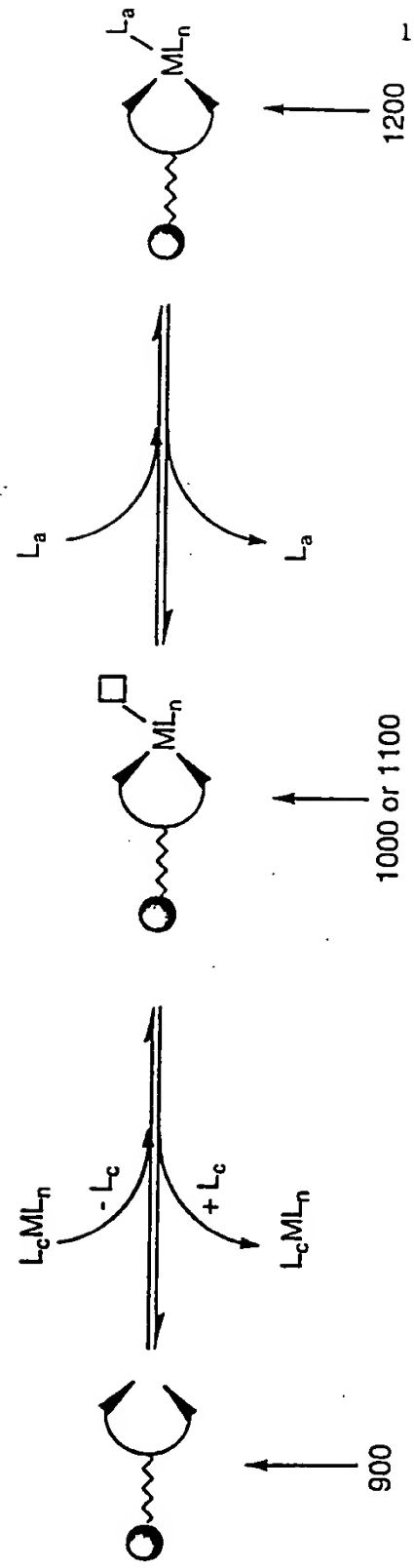


Figure 10

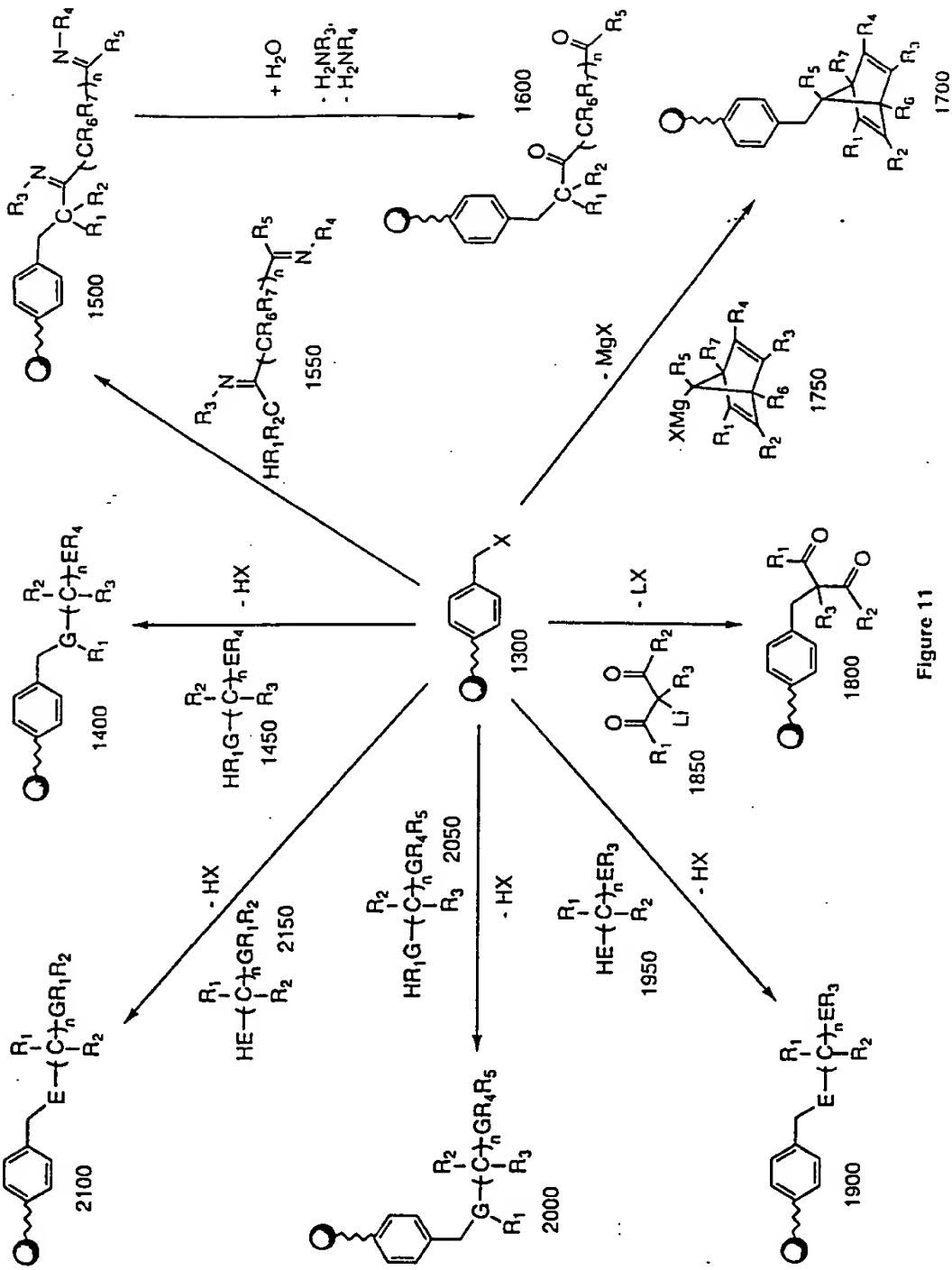

+ H2O
- H2NR3, - H2NR4
1600
1700
1500
1550
- MgX
1750
1400
- HX
1450
- LX
1300
1800
1850
- HX
2150
- HX
2050
- HX
1950
2100
2000
1900

Figure 11

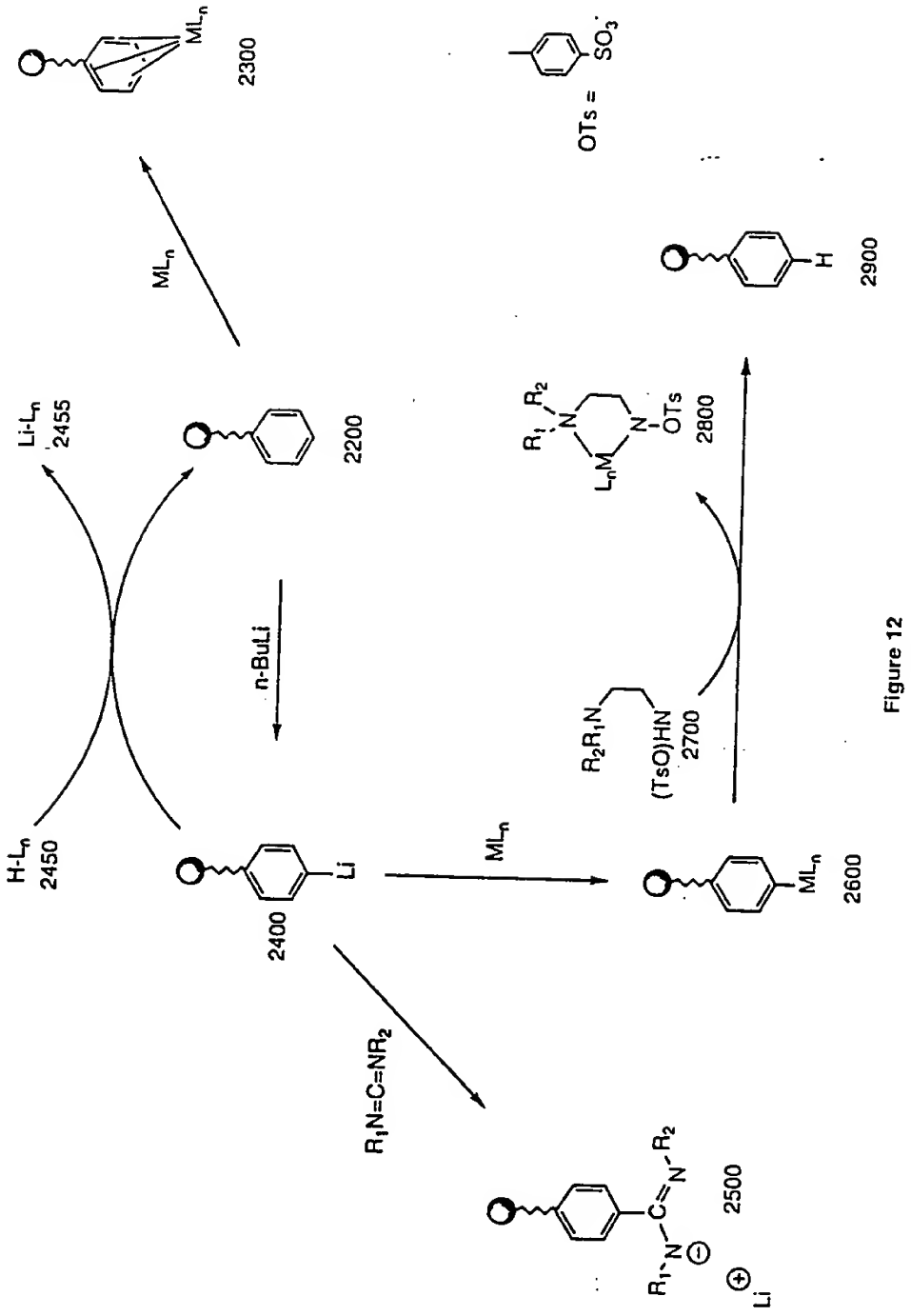

ML$_n$
2300
OTs = SO$_3$
ML$_n$
H
2900
Li-L$_n$
2455
2200
R$_1$ R$_2$
N
N
L$_n$M
OTs
2800
n-BuLi
R$_2$R$_1$N
(TsO)HN
2700
H-L$_n$
2450
Li
2400
ML$_n$
ML$_n$
2600
R$_1$N=C=NR$_2$
R$_2$
N
C
R$_1$
N
2500
Li

Figure 12

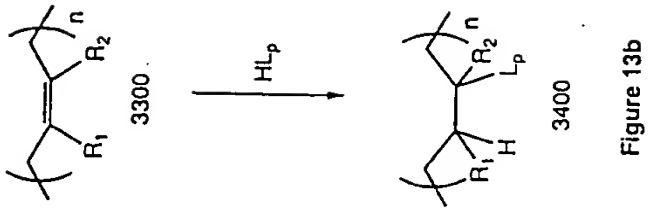


Figure 13b

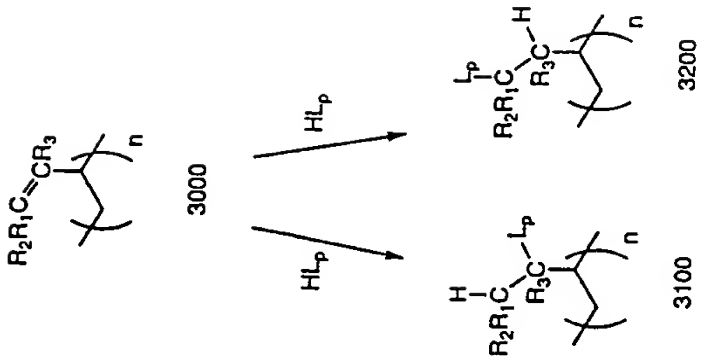


Figure 13a

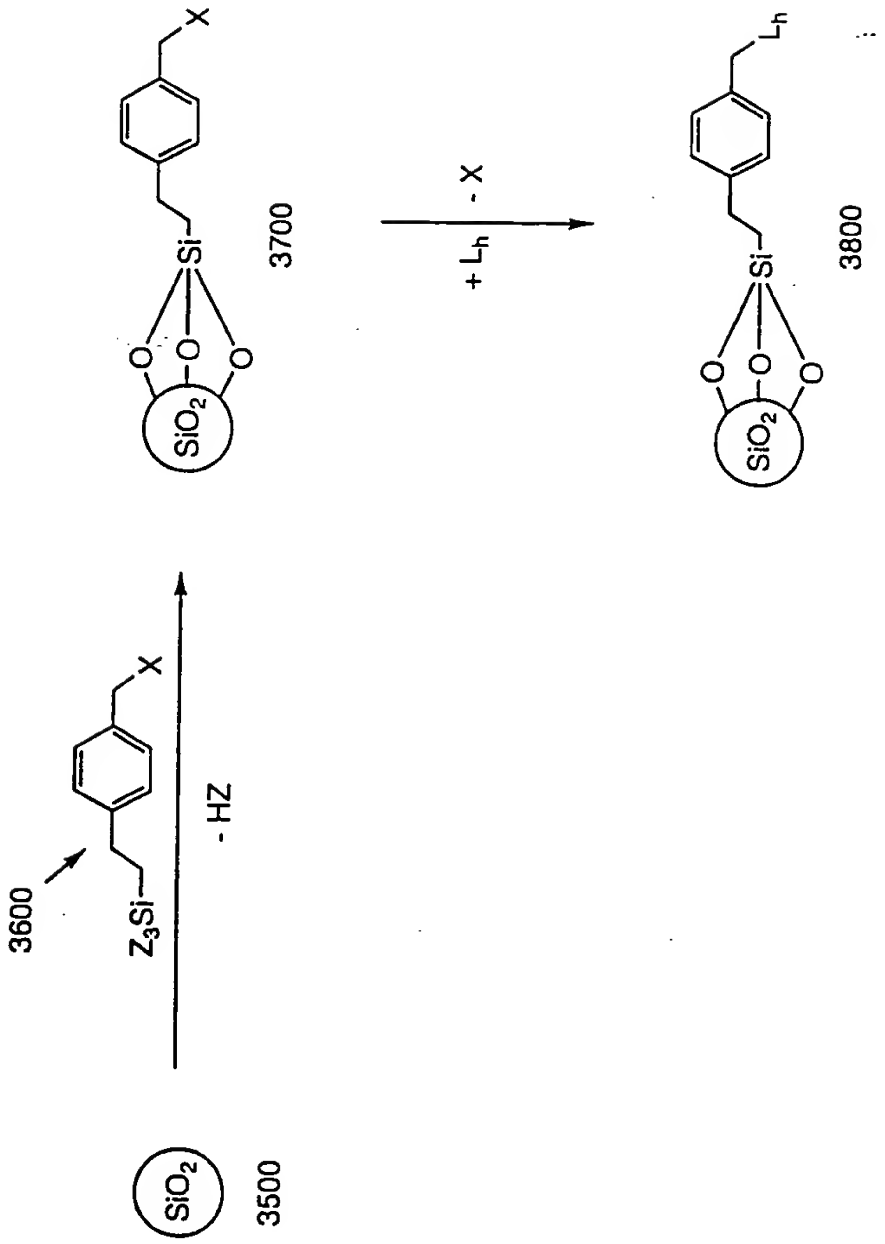


Figure 14

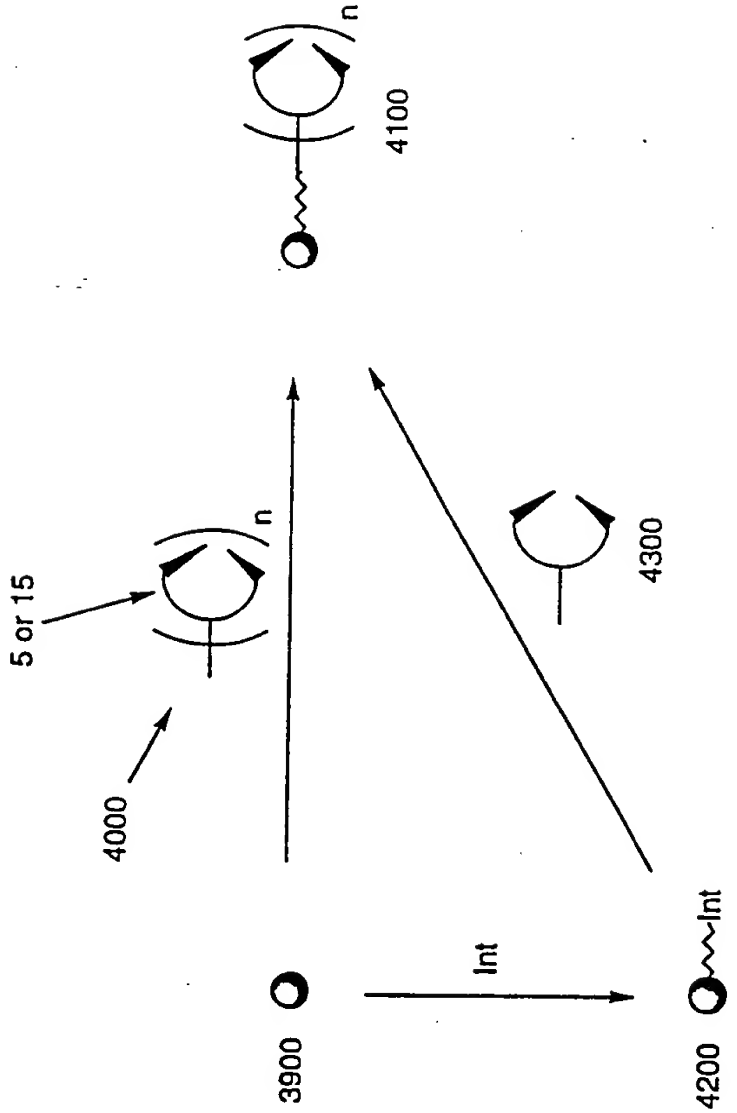


Figure 15

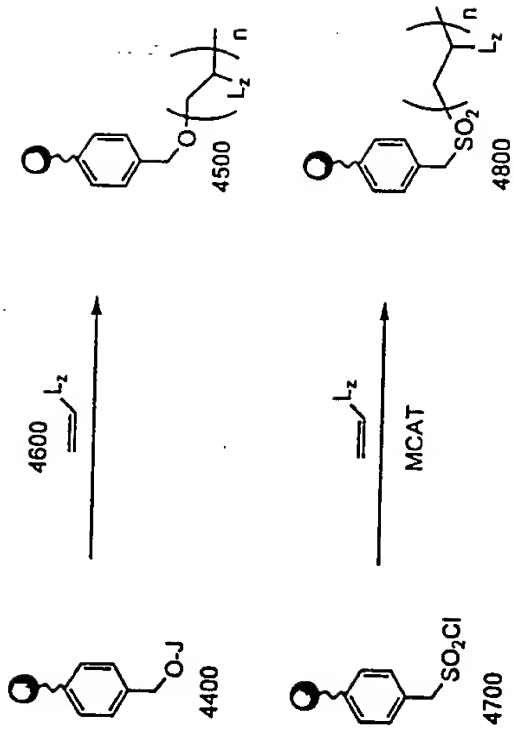


Figure 16a

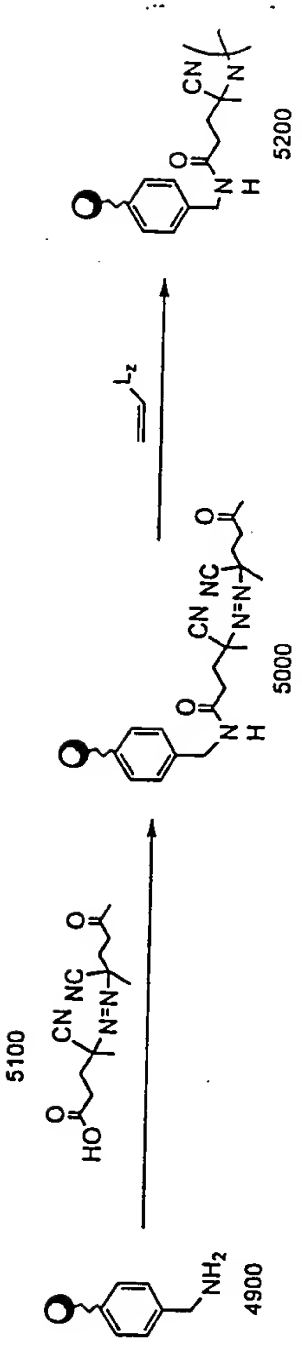


Figure 16b

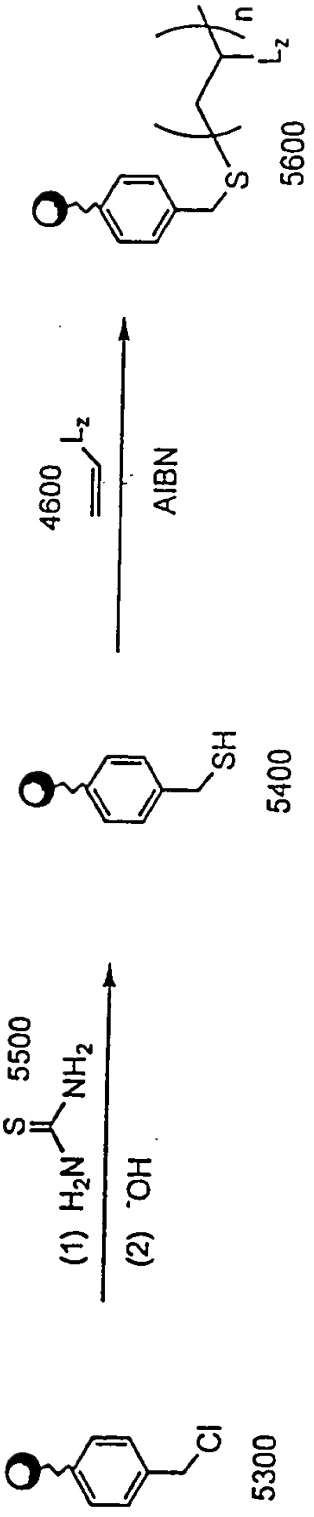


Figure 16c

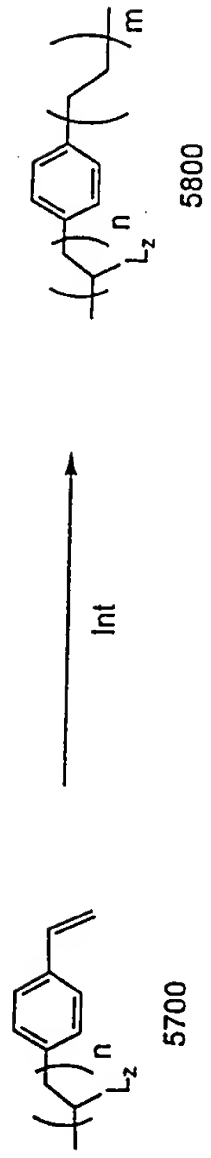


Figure 16d

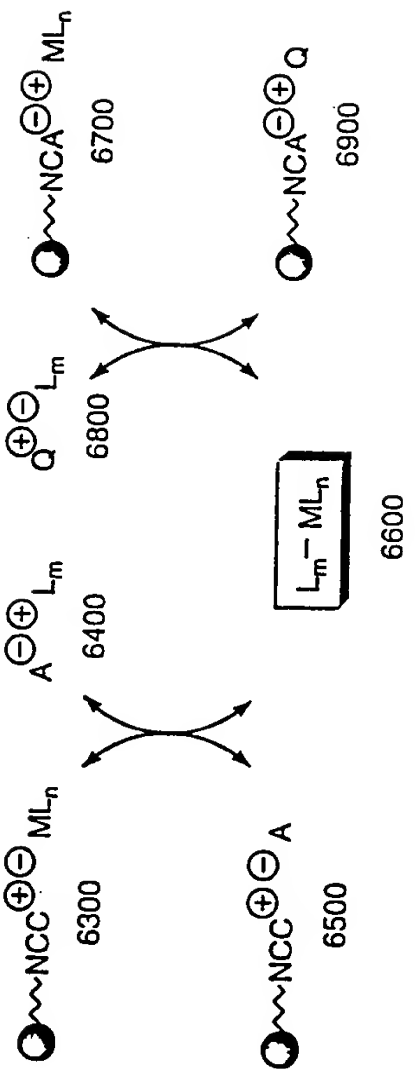

NCC⊕⊖ MLn
6300
A⊖⊕ Lm
6400
NCC⊕⊖ A
6500
Lm– MLn
6600
Q⊕⊖ Lm
6800
NCA⊖⊕ MLn
6700
NCA⊖⊕ Q
6900

Figure 17

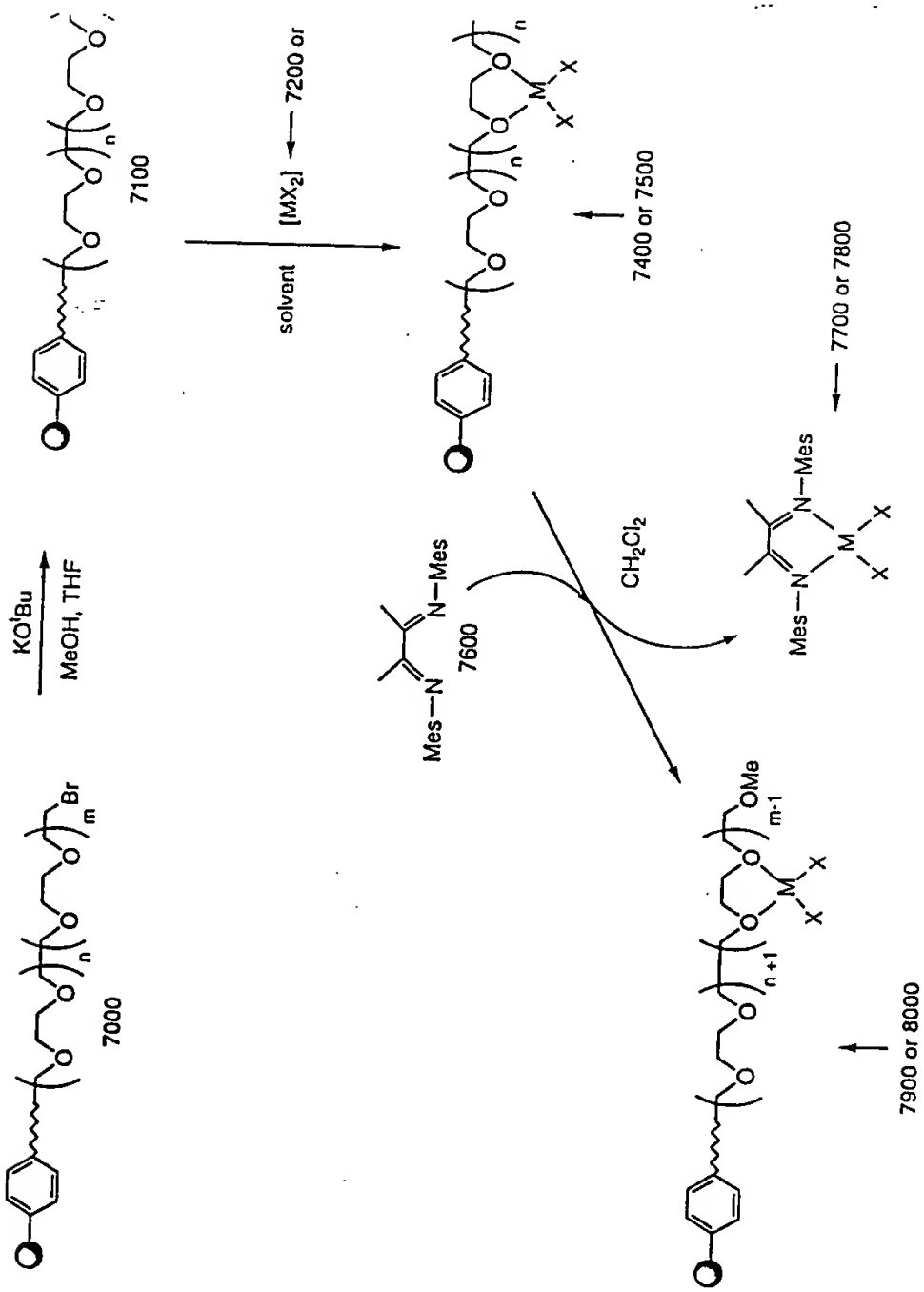

KO'Bu
MeOH, THF
7000
7100
solvent
[MX2] — 7200 or
7400 or 7500
7600
Mes—N
N—Mes
CH2Cl2
7700 or 7800
7900 or 8000

Figure 18

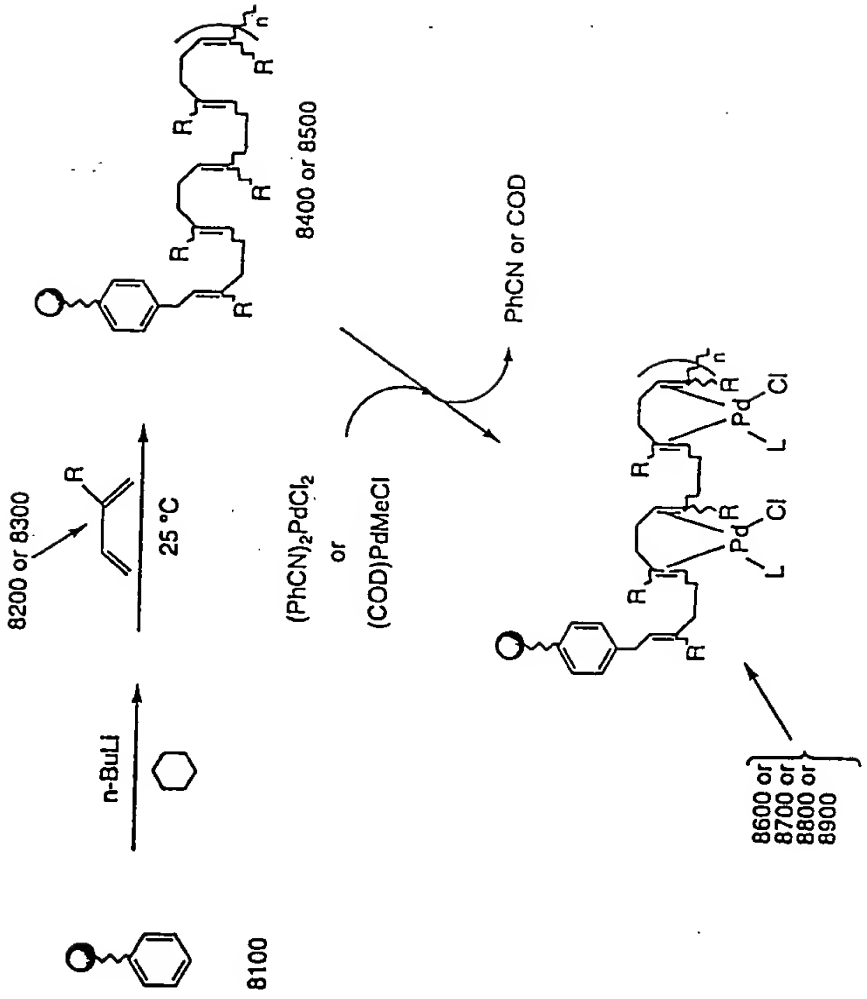

8100
n-BuLi
8200 or 8300
25 °C
(PhCN)2PdCl2
or
(COD)PdMeCl
PhCN or COD
8400 or 8500
8600 or
8700 or
8800 or
8900

Figure 19

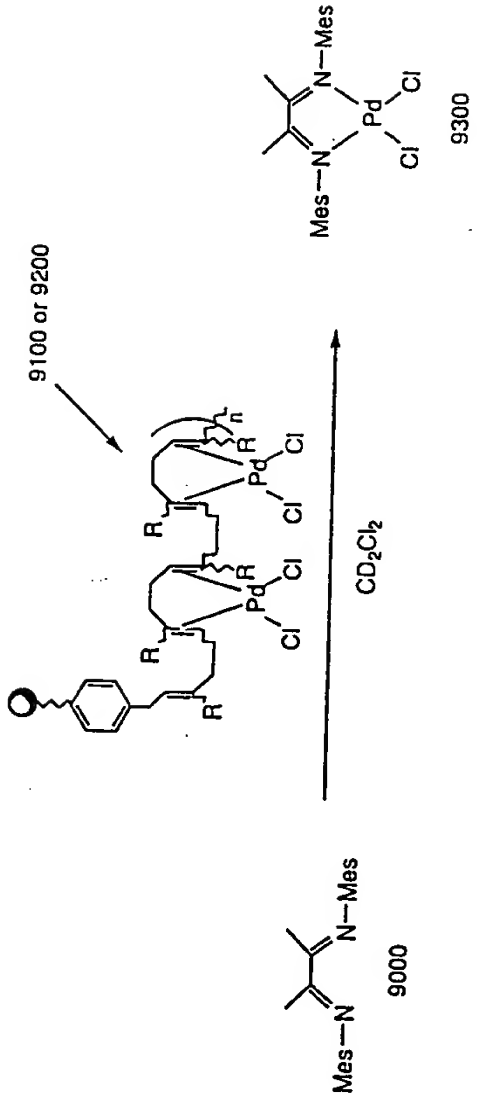
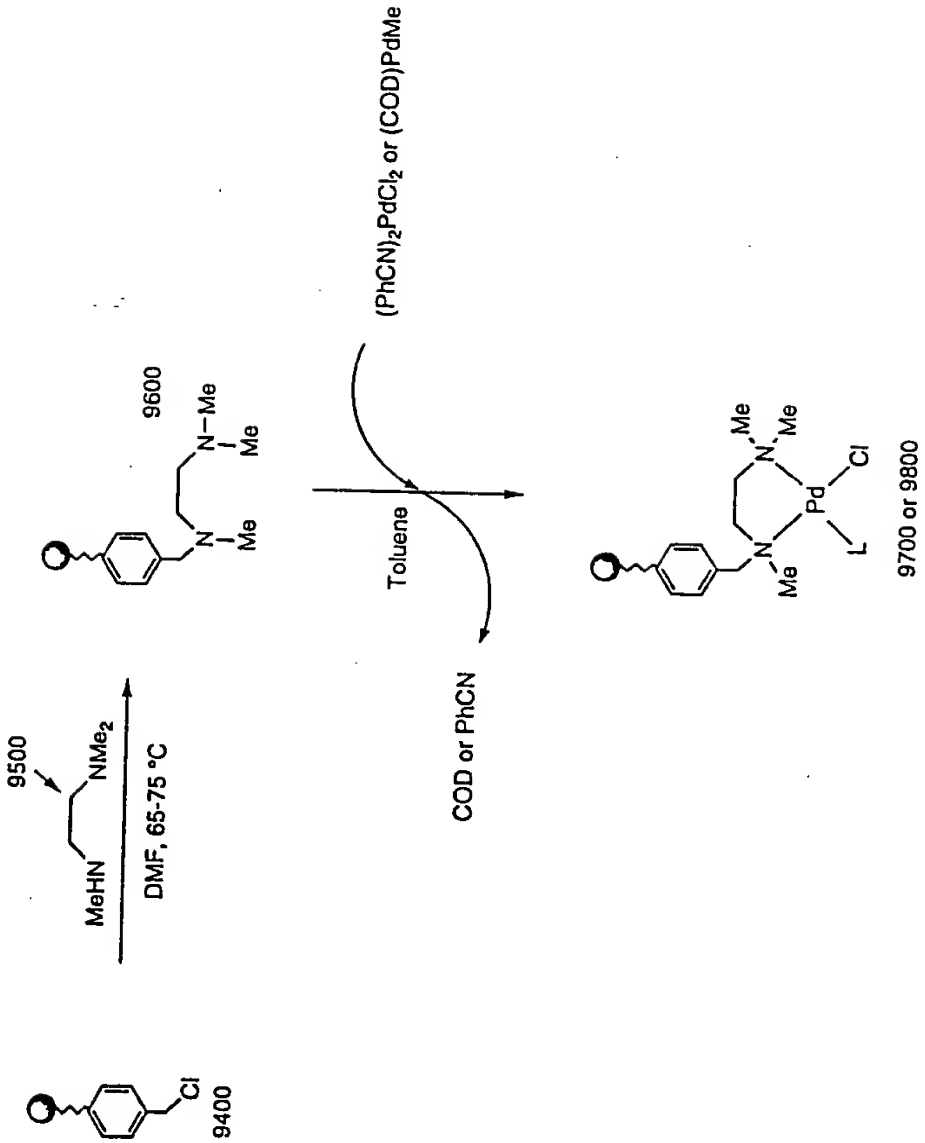


Figure 20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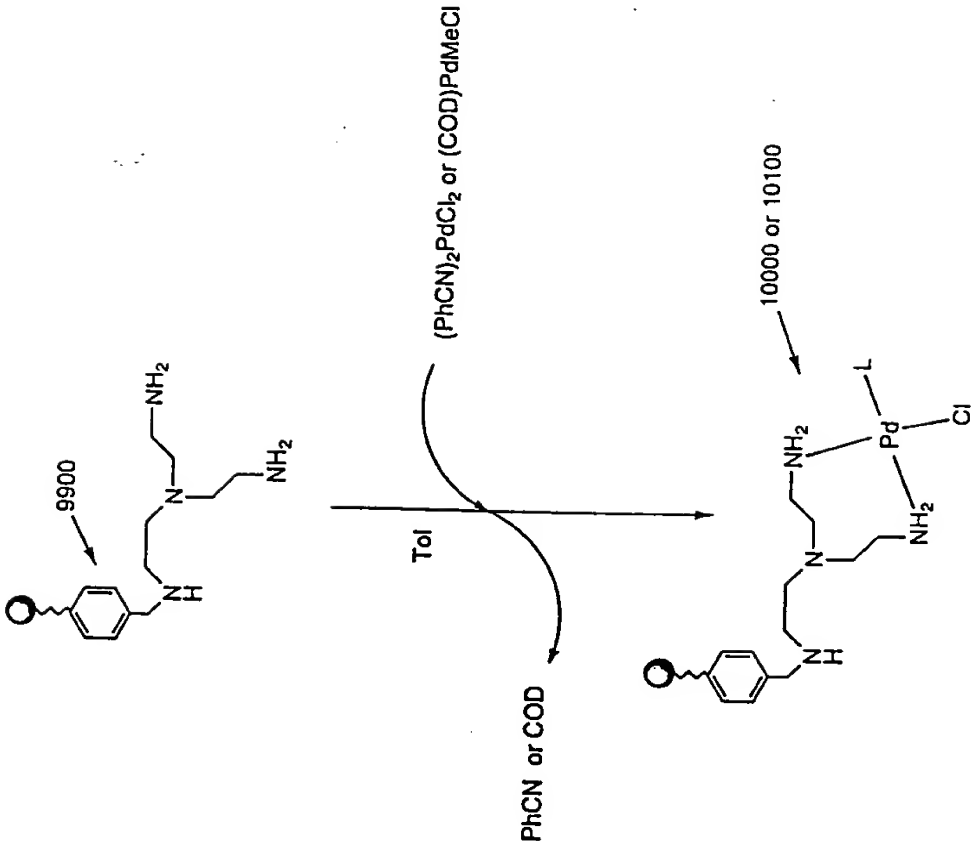
Cl
9500
NMe2
MeHN
DMF, 65-75 °C
9600
N–Me
Me
N–Me
(PhCN)2PdCl2 or (COD)PdMe
Toluene
COD or PhCN
Me
N
Me
Pd
Cl
L
N
Me
9700 or 9800

Figure 21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NH2
N
NH2
NH
Tol
(PhCN)2PdCl2 or (COD)PdMeCl
PhCN or COD
10000 or 10100
L
Pd
Cl
NH2
NH2
N
NH

Figure 22

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/US 98/10863

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F19/00 C07B61/00 B01J19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F C07B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 98 03521 A (SYMYX TECHNOLOGIES) 29 January 1998 cited in the application see the whole document ---	1-111
A	WO 96 11878 A (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 25 April 1996 cited in the application see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 October 1998	06/11/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rinkel, L

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 98/10863

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9803521 A	29-01-1998	AU 3741897 A	10-02-1998
		AU 4673497 A	05-05-1998
		AU 4749397 A	05-05-1998
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		AU 4902497 A	05-05-1998
		WO 9815969 A	16-04-1998
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		WO 9815805 A	16-04-1998
WO 9611878 A	25-04-1996	AU 3957795 A	06-05-1996
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